Molecular Architectonic on Metal Surfaces

Johannes V. Barth

Department of Chemistry, and Department of Physics and Astronomy, The University of British Columbia, Vancouver B.C. V6T 1Z4, Canada and Physik Department E20, Technische Universität München, D-85748 Garching, Germany; email: jvb@ph.tum.de

Key Words

Abstract

The engineering of highly organized systems from instructed molecular building blocks opens up new vistas for the control of matter and the exploration of nanodevice concepts. Recent investigations demonstrate that well-defined surfaces provide versatile platforms for steering and monitoring the assembly of molecular nanoarchitectures in exquisite detail. This review delineates the principles of noncovalent synthesis on metal substrates under ultrahigh vacuum conditions and briefly assesses the pertaining terminology—self-assembly, self-organization, and self-organized growth. It presents exemplary scanning-tunneling-microscopy observations, providing atomistic insight into the self-assembly of organic clusters, chains, and superlattices, and the metal-directed assembly of low-dimensional coordination architectures. This review also describes hierarchic-assembly protocols leading to intricate multilevel order. Molecular architectonic on metal surfaces represents a versatile rationale to realize structurally complex nanosystems with specific shape, composition, and functional properties, which bear promise for technological applications.

Nous voyons dans les éléments de la matière morte une tendance spontanée sinon à
l'organisation, au moins à la combinaison. Les éléments s'unissent, se séparent pour
s'unir à d'autres. Ils affectent de certaines formes.[1]

INTRODUCTION

Among mankind's eternal attributes are imagination, drive for innovation, and a cer-
tain desire for control. Notably the command of matter with its arcane relation to the
genesis of life dictated the course of human civilization. Following the development of
atomic-precision scientific tools and a chemistry inspired by nature's sovereign way to
get organized, we are entering a new era in the conception and design of ultimately
small systems. Postmodern societies will need to cope with the looming unprece-
dented mastery of things contributing their share to the manifold twenty-first-century
promises and risks. This is part of nanoscale science and the nascent nanotechnology.

The engineering of materials with molecular-level precision requires adequate
fabrication and characterization methods. A primordial instrument advancing this
field is the scanning tunneling microscope (1). Some 25 years after its invention,
which notably triggered the seminal demonstration of single-atom positioning (2),
the atomistic real-space viewing and handling of adsorbed species on surfaces remain
a fascinating experience. From the beginning, scientists have recognized the unpar-
alleled spatial resolution and versatility of scanning tunneling microscopy (STM)
as assets in the exploration of single molecules (3). In more recent years, the full
development of molecular manipulation, chemical modification, and spectroscopic
capacities enhanced these attributes (4).

While STM and scanning tunneling spectroscopy were brought to perfection, a
striking evolution matured in chemistry. Back in the 1950s, the structure of DNA was
determined in which selective H-bonding stabilizes an intricate double helix, and an
understanding of the subtle assembly pathways of bacteriophages, viruses, and cellular
components emerged. These landmark achievements enlightened the significance of
refined molecular architecture in biological systems, of which insight spurred a major
paradigm shift in chemical-synthesis strategies.

Why not apply the principles expressed in biomolecular organization to the con-
struction of artificial systems? Indeed, in the 1970s, it became clear that with care-
fully designed functional molecular building blocks, weak and selective noncova-
lent linkages program the formation of supramolecular architectures (5). Moreover,
self-assembly mediated by molecular recognition provides unique and convergent
routes to realize ensembles of highly organized systems (5–9). This *ansatz* mimics
the ubiquitous natural supermolecules, whose proper organization and functioning
are essential for life. Over the past decades, scientists have employed a multitude
of molecular building blocks—also designated tectons (10)—to create increasingly
intricate synthetic arrangements (5–14). The variety and intrinsic functionality of the

---

[1]Cited from *Manuscrit trouvé à Saragosse* (Jan Potocki, Edition intégrale, Librairie José Corti 1989; original
text composed around 1800), Trente-huitième journée: Exposé du système de Velazquez. Free translation:
"We recognize in the elements of inanimate matter a spontaneous tendency if not toward organization, at
least toward combination. The elements assemble, separate to join with others. They adopt specific shapes."

tailored constituents stock a rich arsenal of construction motifs, or supramolecular synthons (15), for the engineering of nanostructures and networks.

It is tempting to combine the nanochemical approach toward the control of matter with the nanophysical appliances. However, there is a service charge for the latter in the sense that their operation essentially implies the presence of a support. As a consequence, the noncovalent design of molecular nanoarchitectures on solid surfaces requires the exploration of a special chemical stage. In the following sections, I delineate the principles of molecular architectonic on atomically clean metal substrates. I also demonstrate that supramolecular engineering in two dimensions opens up new avenues for novel nanostructured materials with unique functional properties and as such is a methodology of interest in the current quest for miniaturization, demanding innovative nanofabrication technologies (16, 17). The main emphasis of this review is on systems realized under ultrahigh vacuum conditions, amenable to STM investigations providing exquisite information at the molecular level.

ON THE SEMANTICS OF SELF-PROCESSES

Autonomous order phenomena belong to the most intriguing expressions of nature. They are commonly rationalized in terms of self-processes. However, self-processes are notoriously difficult to assess or define. Notably, the conceptual ideas underlying self-assembly, self-organization, and related processes—if appreciated at all—are subject to sensible variations across scientific communities. The current confusion is lamentable, and introducing a new terminology may be the only potent remedy.

The term self-assembly was coined in the 1960s, remarkably appearing both in the biosciences and the advertisement sector during the same decade. Today it is predominantly used in scientific contexts. Self-assembly is beyond crystallization, formation, or condensation and is firmly rooted in the biological sciences. A primary inspiration was the demonstrated spontaneous association of entire and infectious viruses from their separated nucleid acid and protein components (18, 19). Biological self-assembly, in which complementary molecular units find each other and form a stable complex (sub)system, plays a decisive role in the function and proliferation of living organisms (18). The lessons acquired in this field had a lasting influence on chemistry, and today the self-assembly paradigm represents a leitmotiv in supramolecular science (5–9). Thus self-assembly tout-court is frequently used as a synonym for molecular self-assembly, which is recognized as the primal strategy for noncovalent synthesis of complex systems, typically integrating multiple components with molecular-recognition capacities. The generalization of this concept lies at hand (5, 7, 20), but lacks consensus. Self-assembly is a prerequisite but is insufficient to rationalize the structuring and operating of cellular architectures (21–23). Investigations of phenomena on surfaces commenced with self-assembled monolayers (24) and more recently moved to advanced supramolecular architectures (17, 25–27).

The expression self-organization was initially employed in the late nineteenth century to describe human collective behavior, and today it pertains to cooperative phenomena in general. The first scientific use presumably occurred in the field of psychology. Incidentally, there are authoritative dictionaries that avoid its listing, whereas

Supramolecular synthon: identifiable linkage within supermolecules or organic crystals qualifying as a general bonding motif for synthetic operations

Nanochemistry: chemical strategy aiming at the generation and nanoscale organization of nonbiological structures with large molecular weight

Supramolecular engineering: the harnessing of noncovalent bonding to design supramolecular complexes and networks

Noncovalent synthesis: considerate use of weak intermolecular interactions to synthesize supermolecules with a high degree of structural complexity

online encyclopedias may be sources of inspiration (e.g., **http://wikipedia.org**). Self-organization has a dynamic undertone and addresses the emergence of order from cosmic to macromolecular dimensions in inanimate, biological, and societal systems. In the physicochemical domain, it describes the formation of steady-state structures away from equilibrium (28), which has been similarly recognized as a general principle for cellular organization (22, 23).

Moreover, beyond nonequilibrium thermodynamics, the transition from inanimate matter to living organisms was associated with self-organization as the initial step culminating in the eventual encoding of the total information for life into the genome (29). This view provides a natural link to the aspiration of supramolecular science to create highly organized systems by deliberate chemical programming of molecular species (5, 30). Self-organization in surface chemical systems is exemplarily illustrated by the spatiotemporal pattern formation in oscillatory heterogeneous catalytic reactions (31). Also static mesoscopic patterning or island arrangements expressed in surface reconstructions, molecular layers, or ultrathin film evolution were loosely associated with self-organization.

The distinctive notion of self-organized growth has been employed since the 1990s within the molecular-beam-epitaxy community to describe the mesoscale evolution of regular patterns in semiconductor or metal-epitaxial growth (32, 33). With such systems, strain relaxation and the delicate interplay between thermodynamics and growth kinetics regulate structure formation. Macroscopic correlatives would be snowflakes in their countless variations. According to this perception, self-organization and self-organized growth are fundamentally different processes. This differentiation complements the above expressions and furthermore comprises an interesting parallelism to principles ruling biomimetic synthesis and biomineralization (34).

A potential classification scheme is to associate

1. self-assembly with the spontaneous formation of spatially textured constructs of definite shape, which are stable under equilibrium conditions. Self-assembly can proceed in closed systems integrating clearly identifiable functional units interacting synergetically. The free-energy minimization yields ensembles of identical products, which may even be replicated.
2. self-organized growth with regular arrangements controlled by mesoscale-force fields or kinetic limitations arising in processes accompanying matter accumulation. The resulting structures are uniform to a certain extent but a priori not identical at the atomic or molecular scale.
3. self-organization with spatiotemporal order phenomena in open systems, in which away from thermodynamic-equilibrium energy supply, competing diffusion processes and chemical interactions mediate the formation of dynamic patterns or adaptive structural arrangements.

NONCOVALENT SYNTHESIS IN TWO DIMENSIONS

For the handling of complex molecules on metals, we need to understand adsorption, mobility, and lateral interactions, all of which depend on the substrate atomic environment, chemical nature, and symmetry (3, 27, 35, 36). Only the accurate balancing
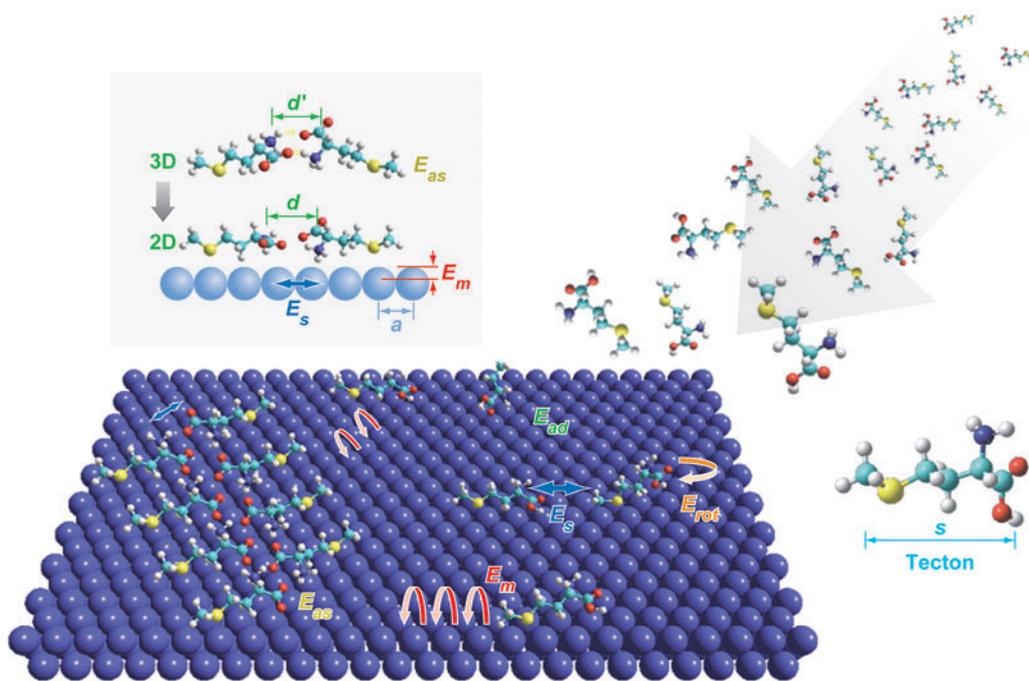
Figure 1

Supramolecular engineering in two dimensions: the substrate atomic lattice is exposed to a
beam of molecular building blocks. Decisive for the assembly of nanoscale architectures are
adsorption (energy E_{ad}), thermal migration and rotational motions (barriers E_m and E_{rot}), and
substrate-mediated and direct lateral interactions (energy E_s and E_{as}). An exemplary tecton
with two functional groups (S atom in *yellow*; N and O in amino group in *red* and *blue*,
respectively) and length s is shown. It self-assembles into the twin chain depicted at the left,
which is stable at thermodynamic equilibrium. The inset illustrates in a side view how surface
atoms (a is the lattice periodicity) can influence the supramolecular synthon characteristics and
the noncovalent-bond length d.

of lateral and surface interactions allows for the emergence of supramolecular order.
To date, scientists notably employed noble-metal and Cu substrates to explore the
aufbau of complex architectures using noncovalent synthesis schemes (17, 25–27).

  Figure 1 illustrates the principles of two-dimensional (2D) supramolecular engi-
neering: A molecular beam is directed onto a well-prepared surface. The tectons—
the given example is an amino acid with length s—adsorb on the substrate (energy
gain E_{ad}), typically in a definite configuration and at specific sites. The coupling to
the atomic lattice confines the molecules and influences the supramolecular syn-
thon characteristics (strength, bond length d) (see **Figure 1** inset). Following sur-
face migration and 2D rotation (thermally activated processes associated with energy
barriers E_m and E_{rot}, respectively), molecular recognition directs noncovalent-bond
formation between functional groups (energy gain E_{as}). Near thermodynamic equi-
librium, distinct molecular nanostructures self-assemble, whereby self-correction can

Table 1 Classification of basic interactions and processes, with associated energy (barrier) and typical distances relevant when functional molecular species are employed to engineer molecular architectures on metal substrates

	Energy range	Distance	Character
Adsorption	$E_{ad} \approx 0.5–10$ eV	$\approx 1.5–3$ Å	Directional, site selective
Surface migration	$E_m \approx 0.05–3$ eV	$\approx 2.5–4$ Å	1D / 2D
Rotational motion	$E_{rot} \sim dim\,(E_m)$	s	2D
Indirect substrate mediated	$E_s \approx 0.001–0.1$ eV	a to nanometerrange	Oscillatory
Reconstruction mediated	$E_s \sim 1$ eV	short	Covalent
van der Waals	$E_{as} \approx 0.02–0.1$ eV	< 1 nm	Nonselective
Hydrogen bonding	$E_{as} \approx 0.05–0.7$ eV	$\approx 1.5–3.5$ Å	Selective, directional
Electrostatic ionic	$E_{as} \approx 0.05–2.5$ eV	Long range	Nonselective
Metal-ligand interactions	$E_{as} \approx 0.5–2$ eV	$\approx 1.5–2.5$ Å	Selective, directional

Surface-specific aspects listed in top five rows. Characteristics of direct intermolecular noncovalent bonding (bottom four rows) are representative for 3D compounds (see References 13, 15, and 37).

eliminate transient defective arrangements. In addition to the direct interactions between functional groups, indirect substrate-mediated interactions are operative (maximum strength E_s), which may influence the mobility and affect the molecular self-assembly. For multicomponent assemblies, we must ensure that transport and interaction characteristics of all components are balanced. To engineer coordination architectures, we need to handle adsorbed molecular tectons and metal adatoms simultaneously. **Table 1** gives an overview of the relevant processes and interactions, associated energy ranges, and bond lengths.

DFT: density-functional theory

The Tecton-Substrate Complex

Molecule-surface interactions are a key issue in the noncovalent synthesis on surfaces. For their comprehensive understanding and control, it is often mandatory to combine complementary experimental techniques and computational modeling. At the current stage the adsorption of complex molecules is a matter of active research (27, 38). For small organic species on metals, bond energies in the range 0.3–5 eV per functional group were concluded (38), strongly depending on substrate reactivity, symmetry, and electronic properties. Typically one is interested in structures stable at 300 K; in other words, to exclude appreciable thermal desorption, the adsorption energy per molecule E_{ad} should exceed ~1 eV. This estimate is based on the desorption rate for an isolated species $\Gamma_{des} = \nu_o \exp[-\beta E^*]$, where ν_o is of the order of 10^{13} s^{-1}, $\beta = [k_B T]^{-1}$, and E^* is the corresponding energy barrier.

Examining the detailed bonding configuration often represents an experimental challenge, in which STM frequently can clarify basic structural aspects, and synchrotron-radiation studies provide complementary insight (38–41). The tectons usually adsorb at specific sites because the functional groups sense the substrate atomic arrangement (38, 39, 41). Density-functional theory (DFT) and other model calculations confirm this idea and provide insight into the bonding characteristics (42–45),

but a shortcoming of DFT is that it fails to properly include van der Waals inter-
actions. The adsorption configuration of molecules that are mainly anchored with
a specific moiety on the substrate may be tunable with the surface concentration
or temperature-induced chemical transformation of functional groups (27, 46, 47),
or the electronic structure of the substrate (48). When flexible species or tectons
with internal degrees of freedom are employed, marked intramolecular distortions
or conformational adaptation can occur (36, 49–52). In special cases even reversible
conformational switching phenomena become apparent (53). Characterizing the ad-
sorption configuration of molecules with multiple internal degrees of freedom is a
real challenge (54, 55). Furthermore, the symmetry reduction associated with the 2D
confinement brings along a rich variety of chirality phenomena, which have been
reviewed at length elsewhere (27, 56).

With appreciable tecton-substrate interactions, rearrangements of the substrate
atomic lattice can occur. In most cases, the driving force for these surface reconstruc-
tions is the energy gain owing to the improved embedding in the modified atomic
environment (57–61). Conversely, naturally reconstructed or artificially patterned
surfaces can provide inhomogenous templates with preferential adsorption sites for
tectons, thus steering their self-assembly (62–66).

Transport and Rotation of Complex Molecules in Two Dimensions

Once adsorbed, the tectons can transport between different bonding sites. When
a unique migration energy barrier E_m for displacements of isolated species exists,
a $\Gamma_s = \nu_s \exp[-\beta E_m]$ rate law is obeyed (provided $k_B T \ll E_m$), whereby one can de-
termine single-molecule hopping rates Γ_s by temperature-controlled STM (67, 68).
For large species, prefactors ν_s in the 10^{10}–10^{14} s^{-1} range were reported (58, 69,
70); in other words, if self-assembly at ambient temperature is desired, E_m should
not exceed ∼0.5 eV. Generally the tectons move between adjacent adsorption sites,
but in exceptional cases, so-called long-jump events over multiple sites occur (70).
The migration barriers are adsorption-configuration dependent (71, 72). Directional
motions prevail on anisotropic surfaces (58, 67, 69, 70). However, complex migration
mechanisms can promote one-dimensional (1D) motion even on isotropic substrates
(73, 74). Furthermore, one can tailor the mobility characteristics of adsorbed tectons
by the considerate modification of terminal moieties (36, 70, 75).

For site-specific bonding, the tectons have a distinct orientation with respect to the
substrate atomic lattice in their minimum-energy configuration, and 2D rotations are
possible. Molecular rotations require thermal activation, analogous to lateral trans-
port. In the simplest case, they imply the overcoming of a unique rotation energy
barrier, whence a rate law applies: $\Gamma_r = \nu_r \exp[-\beta E_r]$, where rotation energy bar-
riers E_r (prefactors ν_r) of the same dimension as E_m (ν_s) are expected. To date, the
characteristics of rotational motions have been quantified only for acetylene (C_2H_2)
adsorbed on Cu(100) (76). Detailed studies for larger species are lacking, although
the order expressed in 2D self-assembly provides ample indirect evidence (17, 26,
68), and STM observations of hexa-*tert*-butyldecacyclene on Cu(100) indicated con-
tinuous rotation of a single molecule laterally confined in a vacancy of an organic

layer (77). Furthermore, the rotational motion of individual trimesic-acid molecules participating in a complexation reaction was monitored by STM on Cu(100) (78). Obviously, lateral transport and rotation may appear as concerted process. Even more intricate 2D-motion schemes imply the cooperative action of multiple intramolecular degrees of freedom for adsorbed nanovehicles (79) or molecular barrows (80).

Substrate-Mediated Interactions

Perturbations of the substrate electronic and strain field induced by adsorbates mediate lateral interactions (81, 82). These so-called indirect interactions can be either of elastic or electronic origin, are oscillatory in nature modulated by a decaying envelope, and typically extend in the 10-Å range. Field-ion-microscopy studies with metal and Si adatom pairs on refractory metals revealed indirect cohesion of $\sim$0.1 eV at the closest distance (81). Quantitative studies for molecular adsorbates are scarce, but STM demonstrated substrate-mediated chaining of oxygen molecules on Ag(110), where the strongest attraction occurs at a distance of two lattice spacings with $E_s \approx 40$ meV (83). Recent studies focused on interactions mediated by surface-state electrons, extending in the range of several nanometers (82). With adsorbed atoms, they are rather weak (milli-electron-volt range) but could be exploited to create a 32-Å hexagonal atomic Ce superlattice on Ag(111) at cryogenic conditions (84). Surface-state-mediated interactions similarly have been invoked regarding adsorbed organic species (85, 86) and possibly promote the mesoscopic organization of 1D superlattices on close-packed noble-metal surfaces (87–89). However, long-range order can be similarly driven by surface strain-field perturbations (17, 90, 91).

A significantly higher energy scale is entered when the substrate lattice undergoes rearrangements driven by tecton-surface interactions. These processes require thermal activation. Depending on the molecular coverage, the substrate reconstructions can be localized (57, 58, 92) or mediate the formation of regular superstructures (59–61, 93). The energies for the associated elementary steps are appreciable (electron-volt range) because disruption of substrate interatomic bonds is involved. Lateral interactions mediated by tecton-driven reconstructions are thus typically much stronger than those originating solely from surface elastic and electronic perturbations (57, 93).

Molecular Recognition and Direct Noncovalent Bonding

In view of the nature of tecton-substrate complexes and their mobility and interaction characteristics described above, clearly a special chemical stage is set for noncovalent synthesis on surfaces. Accordingly, it is a priori impossible to rely on rules and experiences gathered in solution or solid-state environments. Surfaces represent unique playgrounds in which a novel 2D supramolecular chemistry needs to be explored. The substrate chemical influence is reminiscent to that of a solution employed as a three-dimensional (3D) self-assembly medium. Moreover, the molecules' spatial confinement imposes steric constraints for molecular recognition and frequently induces 2D chirality or supramolecular chiral ordering. The interaction with the surface

atomic lattice affects the motion and conformation of the tectons. Moreover, the synthon characteristics per se can be modified. Hydrogen-bonding energetics, distances, and geometrical alignment at metals do not necessarily reflect parameters encountered in three dimensions. The nature of electrostatic interactions can be markedly influenced by screening effects. Besides mediating indirect interactions, the substrate electronic structure also blurs coordination-chemistry concepts (e.g., the identification of oxidation states) in metallosupramolecular surface compounds (78, 94, 95). Additionally, the surface catalytic activity can result in chemical modifications of specific functional groups. For the present purposes, a thorough understanding of these phenomena is important for their control.

In favorable situations—and these are of practical interest and must be identified—the mobile tectons are adsorbed in configurations promoting molecular recognition and the formation of lateral noncovalent bonds. Then the selectivity and directionality provided by hydrogen bonding and metal-ligand interactions, but also bonding schemes based on nonspecific interactions, mediate the self-assembly of low-dimensional nanosystems. The nature and energetics of noncovalent intermolecular bonds on surfaces are rarely known precisely; however, the overall experiences gathered so far indicate that trends established for 3D systems apply. **Table 1** gives a summary, and the following sections comprise illustrations with specific examples. Notably on gold, silver, or copper surfaces, the substrate bonding does not get out of proportion, when suitable tectons are employed.

In all cases, one must consider the omnipresence of van der Waals interactions. They are notably manifested in lamellar structures of flat-lying chain-like hydrocarbon species realized at solid-liquid interfaces (26), or in self-assembled monolayers from alkane thiols (24), but in many cases their weakness prevents a clear understanding of their relevance.

In three dimensions, the selectivity and directionality of hydrogen bonds (96) offer excellent means for noncovalent synthesis (5, 13). Genuine H-bonded nanostructures with distinct shape can similarly be realized on surfaces. Particularly useful are planar-extended π-system tectons with peripheral functional groups. On appropriate substrates, they adsorb in flat-lying geometries favoring lateral molecular recognition. Similar with 3D hydrogen-bonded architectures, cooperativity—i.e., geometrical complementarity promoting the formation of multiple weak linkages (13)—is an important factor in 2D supramolecular engineering. Studies have identified electrostatic interaction as a major factor in hydrogen bonding (15, 96), and in general, charged or polar moieties can be engaged in H-bridges or other electrostatic coupling schemes. Even stronger, albeit nonselective, bonding occurs in ionic self-assembly explored in solution-based systems (37). In three dimensions, the strength of ionic bonds typically exceeds that of H-bridges; however, appreciable screening may interfere on metals. A special electrostatic interaction is the zwitterionic bonding in amino acid or other crystals, which exists similarly on certain surfaces (27, 88).

The coordination of transition metals to tailored ligands provides an alternative versatile approach for the construction of highly organized molecular arrangements (5, 11, 12, 14). An important feature with metal-ligand interactions is that the appreciable bond energies help to obtain robust entities and that the

incorporated metal atoms bestow specific functions (e.g., electronic, magnetic, and catalytic). For the modular assembly of coordination architectures, extended π-system tectons again proved advantageous. One must take care with the handling of the metal atoms, which may have different mobility characteristics, and potentially drive surface intermixing or alloy-formation processes. Because of these complications, metallosupramolecular architectures on surfaces may require nontrivial-synthesis schemes and can frequently not be regarded as self-assembled in the narrower sense. Furthermore, 2D metal-organic engineering provides a promising link to 3D nanoporous metal-organic frameworks and functional coordination polymers (97, 98).

SELF-ASSEMBLY OF ORGANIC SPECIES

Initial studies of H-bond-mediated assembly on surfaces were inspired by the selective base pairing of nucleic acids. A variety of 1D and 2D hydrogen-bonded structures of nucleosides were realized on Cu(111) (99, 100). Lateral H-bonds mediate the chaining of adenine molecules on the anisotropic Cu(110) surface (101), a motif that similarly proved useful for realizing 1D interconnections of porphyrin species immobilized on Cu(111) (102). However, it is challenging to achieve unique routes toward low-dimensional nanostructures using nucleic acids (100, 103).

Figure 2 illustrates the dimensionality tuning of organic assemblies utilizing the classic carboxyl dimer synthon (15) with a series of tectons. For the assembly of two- or four-membered clusters, carboxyphenyl-substituted porphyrins were employed (65). The STM data and models in **Figures 2a,b** demonstrate tectons adsorbing flat on Au(111) and their selective assembly in distinct clusters. When a mono-carboxyphenyl species is used, pairing occurs, whereas four carboxyl bridges stabilize clover-leaf-shaped arrangements with the *bis*-carboxyphenyl species in *cis*-symmetry. Moreover, two conformers exist in each case, reflecting adaptation to the substrate, which were shown to assemble selectively (65). The cluster distribution is strongly influenced by the Au(111) chevron reconstruction (90), which presumably prevents aggregation mediated by van der Waals interactions. The carboxyl pairing is similarly encountered with the ditopic tecton terephthalic acid [1,4-benzene-dicarboxylic acid (TPA)] adsorbed on the same substrate, whereby the hydrogen bonding is reflected in a linear-chaining motif (see **Figure 2c**). However, one cannot achieve a true 1D assembly because weak secondary interactions stabilize a 2D-sheet structure (104). Finally, an open network structure is created with threefold symmetric, tritopic trimesic-acid [1,3,5-benzene-tricarboxylic acid (TMA)] molecules both on hexagonal and square substrates (46, 105, 106). Hence the honeycomb motif identified in 3D TMA organic crystals (13, 15) can be transcribed to metal surfaces.

These examples illustrate how one can tune the shape and symmetry of supramolecular arrangements on surfaces by the considerate use of appropriate functional molecular species. In a similar demonstration, a series of cyanophenyl-substituted porphyrin tectons formed distinct clusters and chains (63). Dimensionality tuning can be sometimes achieved simply by coverage control. Thus for small surface concentrations, discrete molecular clusters evolve with 1-nitronaphtalene on
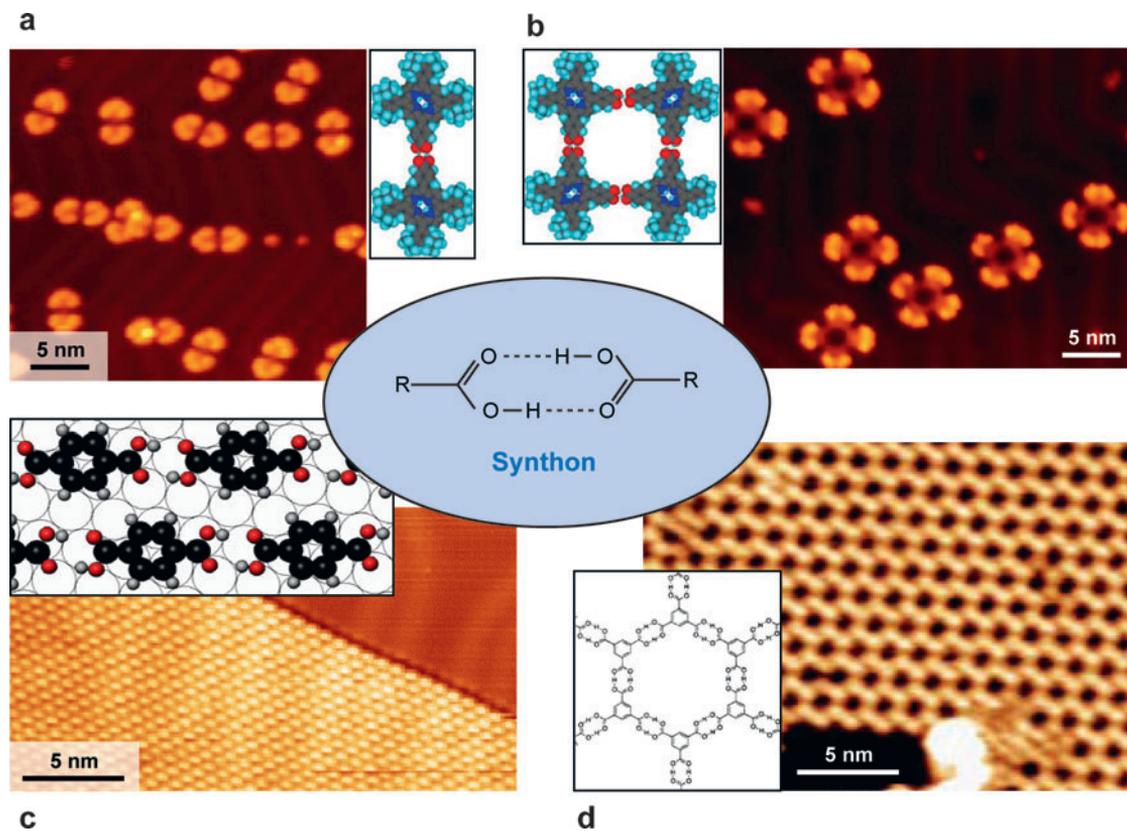
Figure 2

Self-complementary dimerization of carboxylic acid groups as a supramolecular synthon to
engineer supramolecular assemblies on surfaces. (*a*) Two- and (*b*) four-membered clusters of
carboxyphenyl-substituted porphyrins (65) on Au(111). (*c*) A molecular sheet from
terephthalic acid on Au(111) comprising a linear-chain motif (104). (*d*) The open-honeycomb
network structure of a trimesic-acid layer on Ag(111) (106).

Au(111) (62) or cysteine on Au(110) (107) that contrast with the 1D ordering of both
systems encountered at high coverages (62, 93).

Genuine 1D hydrogen-bonded nanogratings in micrometer-sized domains form
on the homogenous Ag(111) surface, reflecting cooperative assembly of the rod-like
tecton 4-[*trans*-2-(pyrid-4-yl-vinyl)]benzoic acid (35, 87), or by using the mesoscopic
pattern of the Au(111) reconstruction as a steering agent (63, 64). Other 1D systems
are zwitterionic-methionine gratings on Ag(111) (*vide infra*) and diphenyl-oxalic-acid
chaining on Au(111) (55).

A different approach to realize regular 2D open-network structures is the bicom-
ponent self-assembly based on the trigonal motif provided by triple hydrogen bonding
between perylene tetracarboxylic di-imide and melamine (108, 109). Finally, a variety
of 2D supramolecular layers has been reported, whose order reflects or can be steered
by the employed tectons' functional end groups (52, 87, 110–112).

The molecular superstructures are generally in registry with the underlying substrate lattice; in other words, adsorption at specific lattice sites prevails. For a rare example in which lateral interactions lead to incommensurate order, see Reference 52. When 2D hydrogen bonds are operative, their lengths are frequently increased in comparison with 3D analogs, which in the simplest cases can be attributed to the preferential occupation of specific adsorption sites (43, 87). Moreover, appreciable length variations of the same 2D H-bond type can occur in the formation of orientational arrangements with different substrate registry (104, 113). This flexibility can be both advantageous or obstructive in supramolecular engineering on surfaces.

A beautiful illustration of cooperativity effects is the self-assembly of guanine on Au(111) (114). The STM image shown in **Figure 3*a*** depicts a regular H-bonded network comprising the distinct guanine-quartet motif highlighted in **Figure 3*b***. A theoretical analysis revealed that this particular unit is stabilized by resonance-assisted hydrogen bonding, in which the formation of multiple H-bridges enhances the bond strength. The respective DFT calculations (see **Figures 3*c,d***) demonstrate an increasing energy per H-bond from 0.22 eV in the dimer to 0.42 eV in the quartet
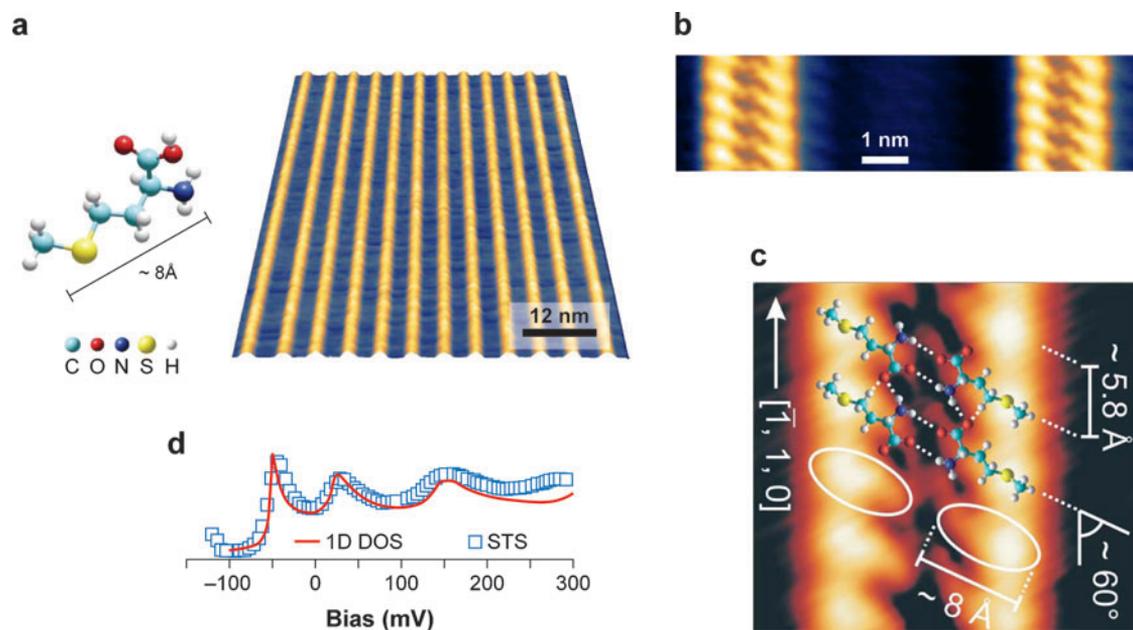
Figure 3

Cooperative hydrogen bonding in the self-assembly of 2D guanine networks on Au(111). (*a*) Regular network of flat-lying molecules comprising quartet arrangements. (*b*) A high-resolution image of the area marked in *a* is shown with a structural model. (*c*) Density-functional theory calculations reveal a formation energy nonlinearly increasing with the number of H-bonds. The associated resonance-assisted charge-density redistribution is illustrated by the inset and the contour diagram in *d*. Figure adapted from Reference 114.
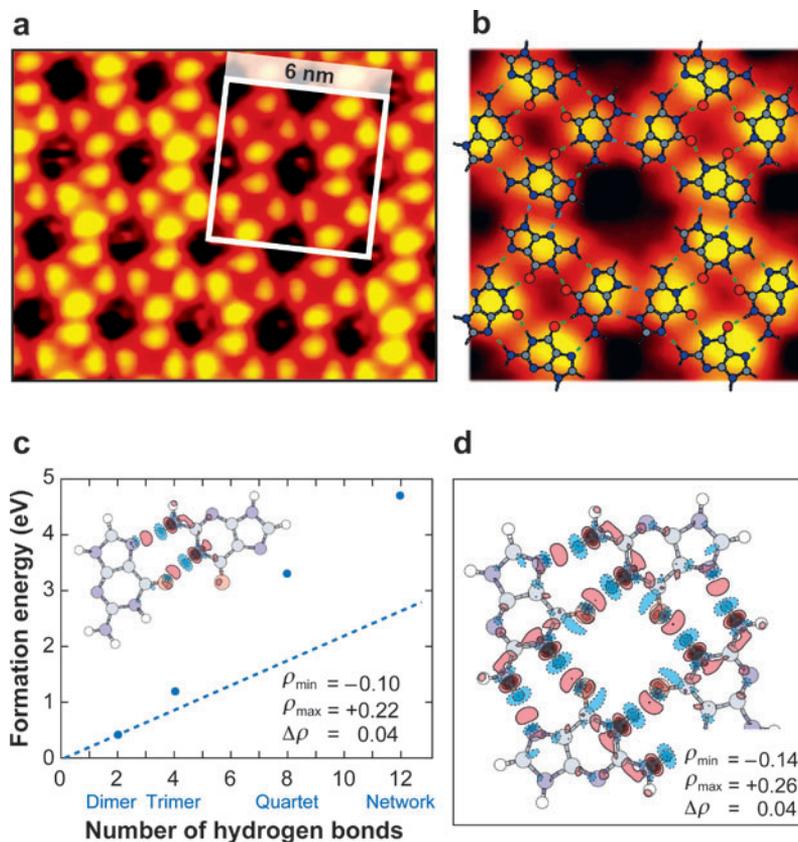
(114). These quartets represent a 2D analog to guanine-based tetramers of biological significance and related cyclic supramolecular complexes (8, 13).

Amino acids represent a further class of biomolecules inherently qualifying for molecular recognition. With the exception of glycine, the basic set of the 20 most common amino acids consists of chiral species, which is of interest in the context of 2D chiral organization (27). For instance, chiroselective recognition occurs in the dimerization of cystein molecules anchored as thiolates on Au(110) (92), and phenyl-glycine decorates adenine chains enantioselectively on Cu(110) (101). In 3D crystals, one typically encounters amino acids as zwitterionic species, and space-integrating investigations demonstrated 2D layers retaining this chemical state (27).

On the frequently employed Cu substrates, amino acids anchored as anionic car-boxylate species prevail (27). By contrast, methionine on Ag(111) undergoes zwitte-rionic self-assembly (88). **Figure 4a** shows an example of the resulting highly regular 1D superlattices whose periodicity can be tuned by the surface concentration. These nanogratings consist of molecular quadruple or twin chains (see **Figures 4b,c**), whose zwitterionic bonding is unambiguously demonstrated by an X-ray photoelectron–spectroscopy analysis of the amino group. The model in **Figure 4c** illustrates the

Figure 4

Zwitterionic self-assembly of methionine molecules on Ag(111). (*a*) Structural model of a single amino acid and perspective view of a nanograting with 60-Å periodicity. (*b*) High-resolution scanning tunneling microscopy image of twin chains stabilized by the zwitterionic-bond motif illustrated in *c*. (*d*) Scanning tunneling spectroscopy on undecorated substrate areas reveals quantum well states reflecting the 1D confinement of Ag(111) surface-state electrons. Figure adapted from References 88 and 89.
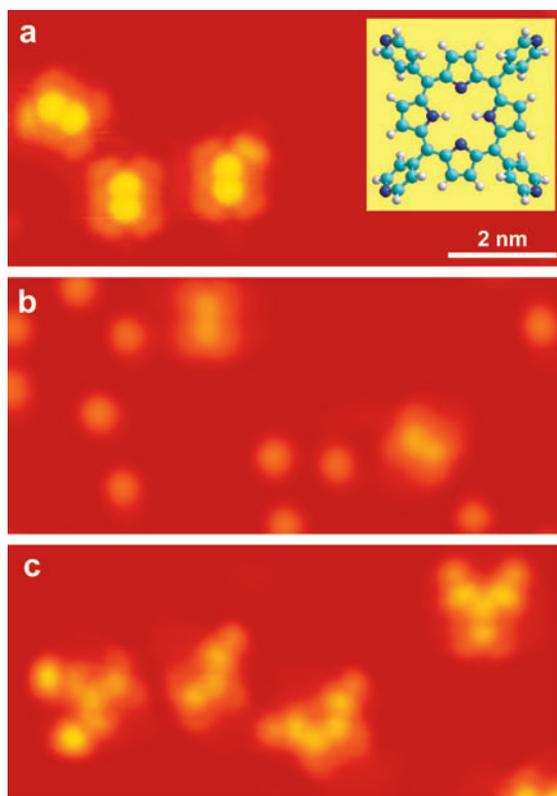
pertaining electrostatic coupling scheme, which was corroborated by molecular-mechanics calculations. The charged moieties mediate both the lateral coupling along the chain directions and the pairing, reminiscent of coupling schemes in related 3D amino-acid sheet structures (88). The mesoscopic ordering into nanogratings suggests long-range substrate-mediated interactions, associated with adsorption-induced strain field or electronic-structure modifications. The latter become apparent in a local quenching of the Ag(111) surface state underneath the methionine assemblies, leading to a striking confinement of the pristine crystal's 2D surface-state electron gas. Scanning tunneling spectroscopy measurements reveal the resulting quantum well states (see **Figure 4***d*) (89). Although the detailed energy balance remains to be disentangled, the findings point to a universal mechanism in the mesoscopic ordering of 1D molecular superlattices realized with different noncovalent-bonding schemes on close-packed noble-metal substrates with surface states (35, 64, 87, 88).

In the methionine zwitterionic assembly described above, overall charge neutrality is implicitly guaranteed; however, on catalytically active substrates, chemical transformations resulting in the ionization of functional moieties may occur. As a consequence, further possibilities (or unwanted pitfalls) appear. On the positive side, thiolate coupling to Au surfaces is commonly used for self-assembled monolayers (24). Also the amino-acid carboxylate anchoring on Cu surfaces mentioned above belongs to this category. Pure carboxylic acids are similarly deprotonated on many catalytically active substrates (e.g., Cu, Pd) in thermally activated processes, which can drive 2D phase transformations (115–118). A particularly elegant example is the use of perylene derivatives on Cu(111), in which a dehydrogenation reaction mediates the formation of autocomplementary tectons that self-assemble in regular honeycomb patterns. The appreciable thermal stability of these networks suggests resonance-assisted hydrogen bonding, similar to the guanine quartets described above (119).

All nanoporous 2D layers are of potential interest as templates to guide the organization of appropriate guest molecules. This has been notably demonstrated by the realization of regular C_{60} arrays using a variety of organic host architectures providing open substrate spaces in H-bonded honeycomb networks (108, 109, 120). Another approach leading to 2D C_{60} patterns is based on self-intermixing phenomena (121, 122). Furthermore, porous layers of cyano-substituted porphyrins can template the complexation and organization of fullerene nanoarrays (123, 124). The anchoring of 3D host molecules on surfaces provides a yet different starting point to realize well-defined spaces for appropriate guest species (60, 125).

HARNESSING METAL-LIGAND INTERACTIONS

In view of highly sophisticated 3D metallosupramolecular chemistry (5, 11, 12, 14), it is appealing to explore coordination-chemistry design principles in 2D. Nevertheless, systematic studies under ultrahigh vacuum were conducted only recently (17, 25, 126, 127). Of central importance thereby is the simultaneous control of metal centers and molecular species, whose mobility characteristics may differ by orders of magnitude. The STM data depicted in **Figure 5** illustrates this issue, demonstrating the interaction of single *tetra*-pyridyl-porphyrin (H_2-TPyP) tectons with iron monomers

on Cu(111). On adsorption, the porphyrin adopts a saddle-shape configuration with the macrocycle residing parallel to the surface, thus providing four lateral exodentate ligands (128). Whereas H_2-TPyP is immobilized at $T <$ 300 K, the migration barrier for adsorbed Fe is small, and single atoms can be observed only on deposition at cryogenic conditions ($T <$ 10 K). At $T \approx 15$ K, the Fe atoms start to move, whence they are readily captured by the pyridyl ligands. The modified imaging characteristics of both Fe and H_2-TPyP indicate marked chemical interaction (see **Figure 5c**).

In a different reaction scheme, one can take advantage of the functional porphyrin macrocycle to create metalloporphyrin compounds and nanoarchitectures in two dimensions. To this end, regular arrays of H_2-TPyP were self-assembled on Ag(111) (52). On exposure to iron monomers supplied by an atomic beam, selective complexation occurs in which the template structure is strictly preserved (129). The STM image reproduced in **Figure 6a** shows a partially developed Fe-TPyP nanoarray. Because the iron atoms arrive at random positions on the surface, the total metalation yield implies lateral movements of Fe on the molecular layer prior to the reaction with the macrocycle. Although the organization of metalloporphyrin layers can also be realized by the evaporation of integral species (110, 123, 124, 129), in situ metalation provides a novel route toward high-purity metalloporphyrin nanoarchitectures and patterned surfaces (129).
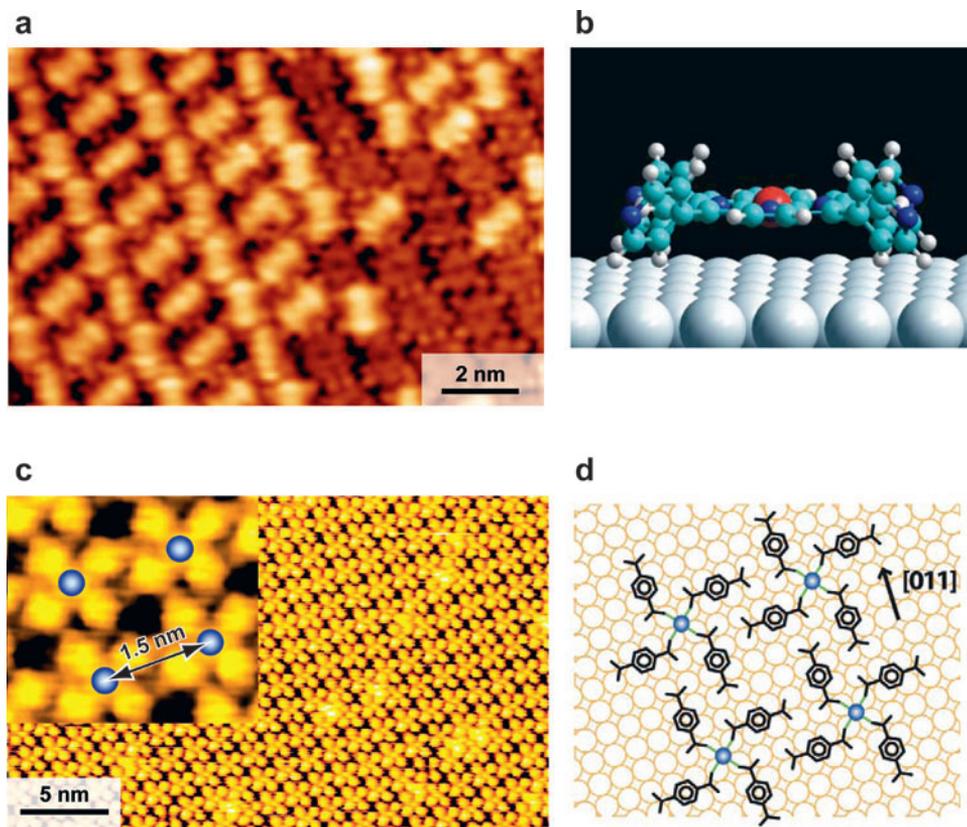
Figure 6

Fabrication of supramolecular arrays comprising single metal atoms. (*a*) Exposing a
self-assembled *tetra*-pyridyl-porphyrin (H$_2$-TPyP) layer to a beam of Fe atoms leads to
metalation: Fe-TPyP nanoarrays form. The bright elongated protrusions reflect iron uptake at
the porphyrin macrocycle, as illustrated in the structure model (*b*) (129). (*c,d*) Mononuclear
Fe(TPA)$_4$ clover-leaf compounds from Fe-directed assembly of terephthalate organized in
regular superlattices on Cu(100) (130, 131).

Carboxylates represent a versatile class of tectons to engineer robust 3D metal-
organic frameworks or functional coordination polymers (97, 98). One can sim-
ilarly use metal-carboxylate coupling schemes on appropriate substrates to tailor
coordination architectures in two dimensions. A series of investigations demon-
strated the construction of mononuclear metal-carboxylate clusters, polymeric co-
ordination chains, and fully reticulated networks based on polyfunctional exodentate
benzoic-acid species. These findings give insight into the principles underlying the
complexation of carboxylates and transition-metal centers on surfaces and illustrate
their potential for rational 2D metallosupramolecular engineering. For instance, the
monitoring of single complexation-reaction events allows one to quantitatively un-
derstand the formation, energetics, and dynamics of individual clover-leaf-shaped

Cu-TMA carboxylate compounds on Cu(100) (78). With this system, the metal centers were furnished by the Cu substrate via thermally activated step evaporation. The Cu adatoms are simultaneously potential agents for deprotonation of the functional carboxylic-acid moieties engaged in the complexation reaction (78, 106). That is, the hydrogen-bonded networks assembled at low temperatures, at which the deprotonation reaction is inhibited, can be transformed into metal-organic arrangements by the catalytic activity of the substrate (46).

One can achieve the synthesis of distinct carboxylate compounds and regular metal-organic coordination networks with specific topologies and a high-structural stability by the sequential deposition of mellitic-acid tectons and Fe atoms on the square Cu(100) substrate. For instance, TMA molecules react with Fe centers to form mononuclear Fe(TMA)$_4$ carboxylate compounds, which are more compact and stable than their Cu counterparts (132). Such complexes arrange into perfect arrays, when linkers providing linear functionalities are used, such as 1,2,4-benzenetricarboxylic acid [trimellitic acid (TMLA)] or TPA. **Figure 6c** shows an example of the arrays built with the Fe(TPA)$_4$ mononuclear compound (130), which are isomorphological to Fe(TMLA)$_4$/Cu(100) superlattices (131). The individual Fe centers span a (6×6)-unit cell (see inset in **Figure 6c**), and this square array extends over entire substrate terraces. The perfect long-range organization in a commensurate superstructure is presumably stabilized by secondary intercomplex carboxylate-phenyl hydrogen bonds (see model in **Figure 6d**).

By utilizing TMLA- or TPA-organic-precursor layers, different types of regular-coordination networks evolve, whose degree of reticulation depends on the Fe concentration (126, 127). This allows the realization of 1D polymeric ladder-type Fe-TMLA structures (126), which are related to Fe-TMA coordination chains obtained on the anisotropic Cu(110) surface (133). In the absence of metal-center deficiency, a full reticulation occurs, in which carboxylate-bridged di-iron centers are recognized as essential coupling motifs (126, 127, 130). The resulting open 2D networks comprise nanocavities with distinct shape and size, which one can employ to selectively host other molecular species, such as C$_{60}$ (127). The cavities' reactivity depends on the presence of molecular side groups, and their size can be increased with higher tecton analogs, such as 1,4'-biphenyldicarboxylic acid or [1,1';4',1'']-terphenyl-4,4''-dicarboxylic acid (127, 134). Moreover, using dissymmetric carboxylpyridyl instead of symmetric dicarboxylato species allows one to steer the network topology (134).

Figure 7a depicts an example Fe-TPA network structure (130). It resides commensurate on Cu(100) with a (6×4)-unit cell. DFT calculations reproduce the main features appearing in the STM data (see **Figure 7c**) and provide an atomistic description of the respective electronic and geometrical structure (95). The corresponding model in **Figure 7b** shows a close-up view of the carboxylate-bridged di-iron center. DFT indicates Fe–O bond lengths of 2.01 (equatorial) and 2.24 (axial) Å, respectively, close to values in 3D Fe-carboxylates (95). A further striking consequence of the strong lateral Fe-carboxylate coupling is the modified Fe-substrate bonding distance upon the embedding of the Fe centers in the metal-organic array: Compared
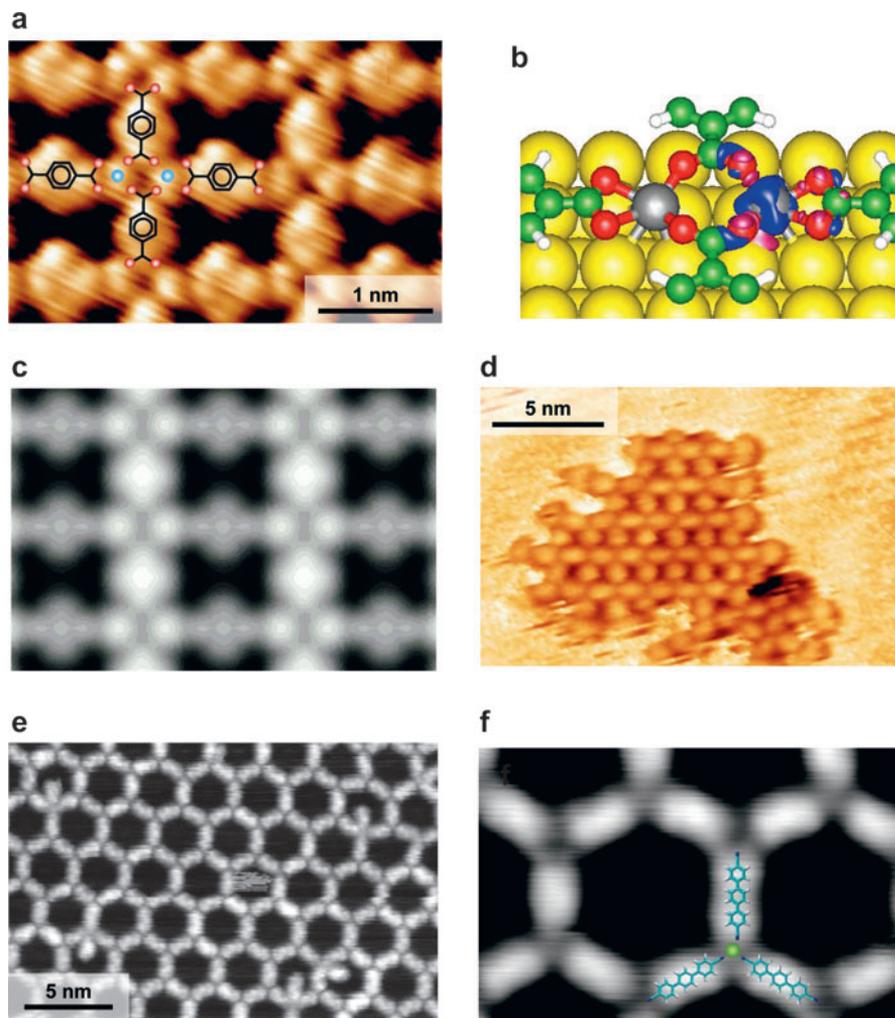
Figure 7

Two-dimensional nanoporous metallosupramolecular grids. (*a*) Rectangular Fe-terephtalate
array on Cu(100) with 1,4-benzenedicarboxylic acid (TPA) tectons and the
carboxylate-bridged di-iron center coupling motif overlaid (130). (*b*) Density-functional
theory (DFT) calculated perspective view of the di-iron unit. The Fe-charge rearrangement
contour levels indicated on the right, drawn with respect to a removed iron atom, are ± 0.004
$e^-/\text{Å}^3$, whereby the colors indicate increased (*magenta*) and decreased (*blue*) electron density,
respectively. Carboxylate moieties and Fe centers lie almost in the same plane ($\Delta z \approx 0.2$ Å),
with the latter slightly displaced away from the fourfold hollow sites, resulting in a lateral
Fe-Fe spacing of 4.4 Å. (*c*) The DFT-based scanning tunneling microscopy (STM) image
simulation agrees with the experimental data (95). (*d*) The Co-terephthalate nanogrid realized
on the quasihexagonal Au(111) substrate is isostructural with its Fe analog on a square lattice
(*a*) (94). (*e*) Co-directed assembly of a metal-organic honeycomb lattice on Ag(111) with
≈ 22-Å cavities. (*f*) Each mononuclear cobalt center coordinates three cyano ligands of ditopic
terphenyl-dicarbonitrile tectons (135).

with isolated Fe adatoms in a fourfold hollow position, those in the Fe-TPA grid are vertically lifted by 0.6 Å. Comparative calculations for the freestanding isostructural 2D Fe-TPA layer signal that the unsupported metal-organic array's properties are close to those of the adsorbed nanogrid; that is, the Cu(100) square atomic lattice represents an excellent template.

Similar rectangular Fe-TPA- or Co-TPA-coordination networks can be realized on the Au(111) quasihexagonal substrate, as shown in **Figure 7d** (94, 136). In conjunction with the DFT results mentioned above, the network formation signals that the nanoporous rectangular grid is the intrinsic expression of 2D cobaltous or ferrous terephthalate sheets, which can override the templating influence of smooth substrates of different symmetry, leading merely to domain-size limitations on Au(111) (94). Further DFT calculations addressed the relative energetics controlling their formation and revealed general trends for the metal-carboxylation reaction displayed by different transition metals (Fe, Co, Ni, Cu, and Au). The driving forces for metal-terephthalate formation on Au(111) are determined primarily by the strength of the metal-carboxylate bond, which is maximum for Co (94).

The Co-directed assembly of ditopic cyano-terminated terphenyl tectons leads to networks comprising trigonal mononuclear nodes. This is illustrated by the hexagonal Co-terphenyl-dicarbonitrile superlattice realized on Ag(111) (see **Figures 7e,f**), in which each metal center coordinates three cyano ligands, and a nanoporous metal-organic layer with ≈22-Å cavities is formed (135). The encountered threefold Co-cyano coordination is a unique feature of the 2D system.

A common characteristic of all 2D metal-organic architectures presented is that they feature coordinatively unsaturated metal centers, which are of interest for their potential functional properties or for extending network design to three dimensions. Complementary X-ray absorption spectroscopy experiments for the Fe(TPA)$_4$ nanoarrays corroborate that true coordination bonds form between Fe and carboxylate ligands, which allows for tuning the electronic and magnetic state of the metal centers. Partial uncoupling of the Fe metallic bond with the substrate leads to effective control of the magnitude of the spin and orbital moment, as well as in-plane, out-of-plane magnetic anisotropy via modifications of the ligand field (137).

HIERARCHIC-ASSEMBLY PROTOCOLS

Organizational hierarchies are abundant in biological systems and biomaterials such as proteins, viruses, or biogenic crystals (34). In a similar way, one encounters distinct levels of structural hierarchies and complexity in artificial supramolecular systems (12). An intriguing strategy that needs further exploration concerns hierarchic order in low-dimensional molecular architectures on surfaces, i.e., the principles governing the transition between primary (molecular) tectons and final mesoscale systems. Achieving long-range order over multiple length scales is essential if the properties of these assemblies are to be harnessed on the macroscopic level. The control of mesoscale self-assembly is thus crucial for improved fabrication and integration of functional nanosystems. Experimental evidence for hierarchic assembly on surfaces
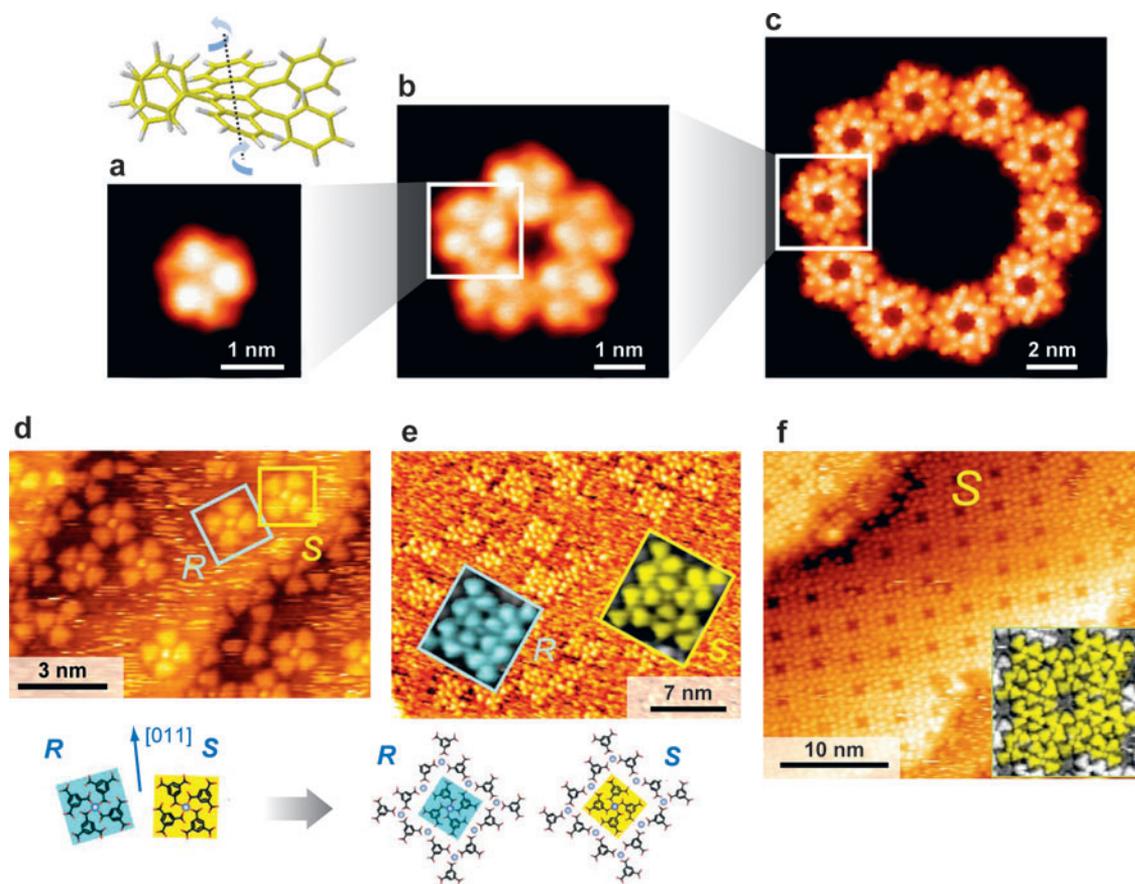
Figure 8

Hierarchic assembly of structures with multilevel order. (*a–c*) Rubrene single molecule, pentameric cluster, and supramolecular decagons observed on Au(111) at low temperatures. (*d–f*) Sequential *aufbau* of robust Fe-trimesate array on Cu(100). The mononuclear Fe-TMA$_4$ clusters (*d*) are nuclei for the assembly of Fe-TMA nanogrids (*e*), which eventually combine into a porous-layer structure (*f*). Insets in *e* and *f* highlight details of the molecular arrangement. The models illustrate the two mirror-symmetric representations labeled *R* and *S*, respectively, which exist at all levels. Figure adapted from References 138 and 139.

reveals intriguing ordering scenarios; however, the present understanding is too limited to establish a conceptual basis for this important domain.

The examples in **Figure 8** illustrate hierarchic order in two dimensions for both organic and metallosupramolecular architectures. The flexible rubrene molecule depicted in **Figure 8a** adsorbs on the Au(111) in an inclined configuration (140). At low coverages, five-membered supermolecules with a 1-nm radius evolve (see **Figure 8b**) (138). They exhibit an unusual pentameric symmetry, are 2D chiral, and assemble in higher-level organizations, such as buckled chains and notably the regular decagon

rings shown in **Figure 8c**. The flexibility of the tecton seems decisive in the underlying bonding scheme mediated by weak van der Waals and H-bonds, whose details remain an open question (140).

Whereas regular patterning could not be achieved with rubrene pentamers, the stronger metal-ligand coupling between Fe centers and TMA molecules mediates the successive *aufbau* of rather robust structures with increasing complexity on Cu(100) (139). By carefully tuning constituent concentration and temperature, the hierarchic assembly can be steered. Initially, the primary building blocks react with Fe centers to form the mononuclear $Fe(TMA)_4$ clover-leaf clusters depicted in **Figure 8d** (132). They appear in two mirror-symmetric configurations and are more compact and stable than their Cu-centered counterparts (78). These secondary complexes in turn are antecedents for tertiary polynuclear nanogrids, representing the motifs that, in a final stage, are organized in 2D mesoscale networks comprising a regular arrangement of homochiral nanocavities (see **Figure 8f**). These nanocavities present identically shaped ≈1-nm diameter hosts, equally spaced by 3.43 nm and functionalized by eight carboxylate groups, which were successfully employed to selectively and reversibly adsorb a series of guest species, including C_{60} and small biomolecules (141). An even more intricate assembly scheme was required to achieve the combination of single nanoporous coordination structures to a polymeric macromolecule composed of *bis*-terpyridine tectons, coordinating 36 Ru and 6 Fe atoms (142).

A further aspect in multilevel supramolecular ordering is the fit of the molecular assemblies to the substrate. This became notably apparent in films of H-bonded *bis*-urea-substituted toluene on Au(111) (143). At the onset of the ordering process, randomly oriented tecton pairs are found, indicating that the coupling to the surface is fairly weak. Cooperative behavior of large supramolecular assemblies consisting of H-bonded polymers then leads to a quasiepitaxial interlocking with the substrate lattice, which occurs without perturbing either the pairing or the underlying reconstruction.

Textured surfaces represent a yet different road toward hierarchic organization. For instance, self-organized growth of Fe or Co on reconstructed Au(111) provides a means to create arrays of transition-metal islands. By tuning the local-reaction conditions with co-deposited terephthalate linker molecules, one can synthesize distinct low-dimensional metallosupramolecular systems, including the regularly spaced Fe-terephthalate ribbons depicted in **Figure 9** (94, 136). The corresponding gratings reflect the substrate chevron pattern (90), with their extension only limited by the terrace morphology (136). They are of interest as template structure, similar to the mesoscopically ordered O/Cu(110) striped phase, a Cu-O superstructure (91), which was successfully employed to guide the positioning and orientation of single complex molecules (66). In a related approach, vicinal surfaces were shown to present regular 1D step arrays that steer the assembly of bicomponent supramolecular wires and ribbons (144).

All the findings reveal that methodologies employing hierarchic assembly protocols bear promise to achieve mesoscale order. They are conceivable for a great variety of systems and can be applied to substrates with different symmetries, as well as physical and chemical properties.
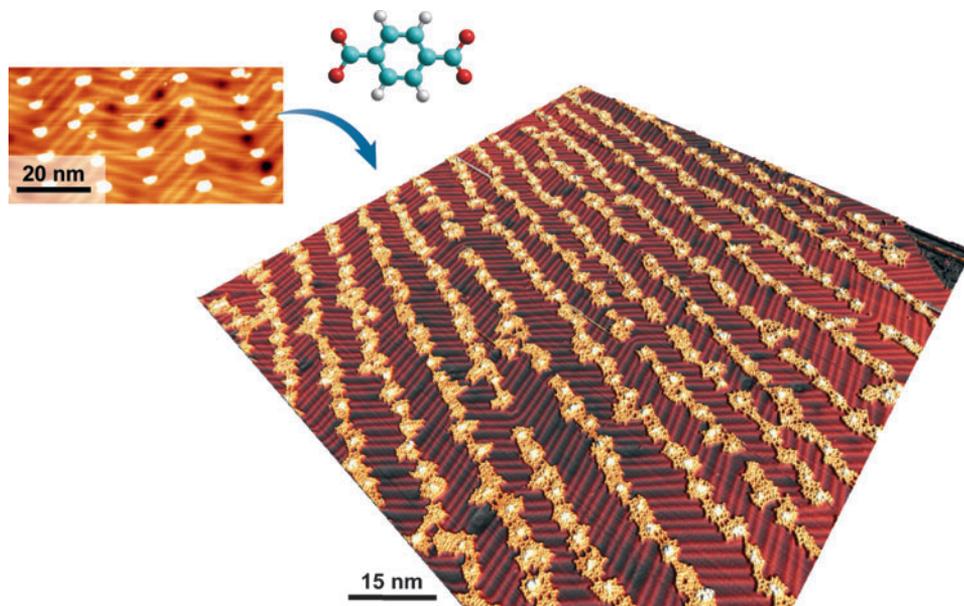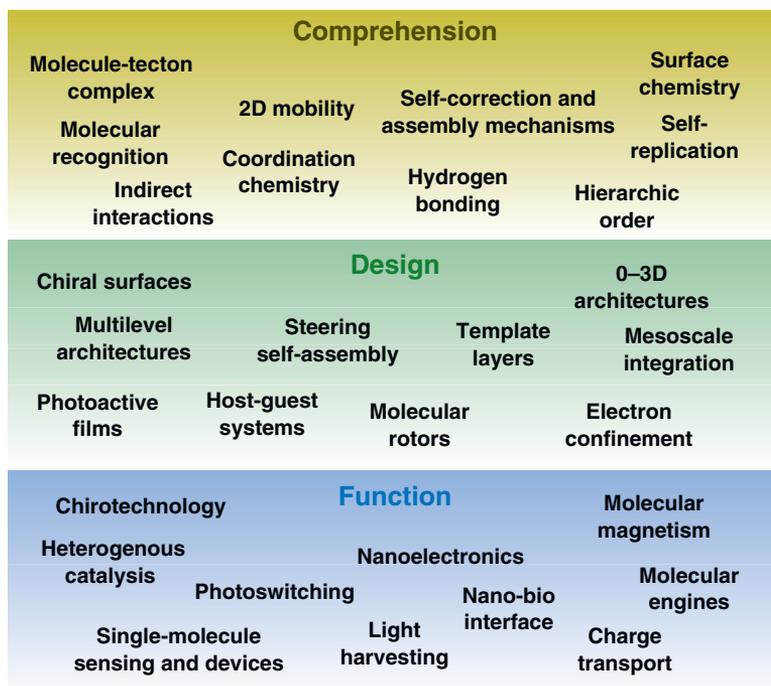
Figure 9

Combination of nanopatterning and controlled metal-organic assembly to process
prestructured metallic templates. Following self-organized growth of Fe nanoarrays on the
reconstructed Au(111) surface (*upper left*), mesoscopic organization of metallosupramolecular
Fe-terephthalate ribbons is achieved by controlling the reaction conditions. Figure adapted
from Reference 136.

PERSPECTIVES FOR DESIGN AND FUNCTION

Designing molecular architectures in reduced dimensions is an elegant and versatile
approach toward the nanoscale control of complex matter (see **Figure 10**). The
advancement of this emerging interdisciplinary domain has been affected by a blend
of curiosity, ingenuity, and serendipity. A large terrain remains to be explored that
seems to be predetermined for exciting discoveries.

Supramolecular engineering on solid surfaces may contribute to establishing fu-
ture nanofabrication schemes and may lead to materials with novel characteristics
as a result of their unique shape and chemical composition. The positioning, inter-
facing, and electronic property control of functional molecules are the quintessence
of molecular electronics (145). Self-assembly of 2D molecular superlattices provides
a novel and versatile strategy to realize low-dimensional quantum-confinement ge-
ometries (89). Evidence for self-replication phenomena in 2D self-assembly exists
(64), and with the adaptation of concepts from 3D systems (9, 13), this could evolve
into a playground of its own. Molecular engineering is also key to sensitizing surfaces
for light harvesting (146).

Guest molecules can be selectively accommodated in the cavities of nanoporous
networks, for example, for sensing purposes, molecular (chiral) recognition, or tem-
plating. Furthermore, the nanocavities provide functional spaces for heterogeneous

Comprehension

Molecule-tecton complex			Surface chemistry
Molecular recognition	2D mobility	Self-correction and assembly mechanisms	Self-replication
Indirect interactions	Coordination chemistry	Hydrogen bonding	Hierarchic order

Design

Chiral surfaces			0–3D architectures
Multilevel architectures	Steering self-assembly	Template layers	Mesoscale integration
Photoactive films	Host-guest systems	Molecular rotors	Electron confinement

Function

Chirotechnology			Molecular magnetism
Heterogenous catalysis		Nanoelectronics	Molecular engines
	Photoswitching	Nano-bio interface	
Single-molecule sensing and devices	Light harvesting		Charge transport

Figure 10

Molecular architectonic on surfaces is bound to advance at three levels: the fundamental understanding of basic interactions and processes, the conceiving and engineering of low-dimensional nanosystems, and the development of nanomaterials and devices performing specific tasks.

catalytic reactions with a well-defined molecular and metallic environment that can be tailored by the tectons, metal centers, and substrate material. Metal-organic networks are similarly appealing for the organization of magnetic atoms in periodic arrangements, in which adequate organic linkers could even mediate magnetic interactions.

2D-patterned molecular arrangements represent nanostructured templates to guide the formation of 3D supramolecular architectures or interconnects to biological systems (147, 148). The employment of biomolecules and bioengineering techniques opens up even wider perspectives (34, 149). Moreover, supramolecular architectures are potential precursors for covalent modification to realize chemically sturdy nanostructures (e.g., by photochemical processes). Finally, supramolecular engineering is a means for the construction or integration of photoswitchable systems, and molecular rotors or engines on surfaces (80, 150).

ACKNOWLEDGMENTS

LITERATURE CITED

1. Binnig G, Rohrer H. 1987. Scanning tunneling microscopy: from birth to adolescence. *Rev. Mod. Phys.* 59:615–25

2. Eigler DM, Schweizer EK. 1990. Positioning single atoms with a scanning tunneling microscope. *Nature* 344:524–26

3. Gimzewski JK, Joachim C. 1999. Nanoscale science of single molecules using local probes. *Science* 283:1683–88

4. Ho W. 2002. Single-molecule chemistry. *J. Chem. Phys.* 117:11033–61

5. Lehn JM. 1995. *Supramolecular Chemistry: Concepts and Perspectives*. Weinheim, Ger.: VCH

6. Whitesides GM, Mathias JP, Seto CT. 1991. Molecular self-assembly and nanochemistry: a chemical strategy for the synthesis of nanostructures. *Science* 254:1312–19

7. Lindsey JS. 1991. Self-assembly in synthetic routes to devices. Biological principles and chemical perspectives: a review. *New J. Chem.* 15:153–80

8. Lawrence DS, Jiang T, Levett M. 1995. Self-assembling supramolecular complexes. *Chem. Rev.* 95:2229–60

9. Philp D, Stoddart JF. 1996. Self-assembly in natural and unnatural systems. *Angew. Chem. Int. Ed. Engl.* 35:1154–96

10. Simard M, Su D, Wuest JD. 1991. Use of hydrogen bonds to control molecular aggregation: self-assembly of three-dimensional networks with large chambers. *J. Am. Chem. Soc.* 113:4696–98

11. Leininger S, Olenyuk B, Stang PJ. 2000. Self-assembly of discrete cyclic nanostructures mediated by transition metals. *Chem. Rev.* 100:853–908

12. Swiegers GF, Malefetse TJ. 2000. New self-assembled structural motifs in coordination chemistry. *Chem. Rev.* 100:3483–538

13. Prins LJ, Reinhoudt DN, Timmerman P. 2001. Noncovalent synthesis using hydrogen bonding. *Angew. Chem. Int. Ed. Engl.* 40:2382–426

14. Holiday BJ, Mirkin CA. 2002. Strategies for the construction of supramolecular compounds through coordination chemistry. *Angew. Chem. Int. Ed. Engl.* 40:2022–43

15. Desiraju GR. 1995. Supramolecular synthons in crystal engineering: a new organic synthesis. *Angew. Chem. Int. Ed. Engl.* 34:2311–27

16. Gates BD, Xu Q, Stewart M, Ryan D, Willson CG, Whitesides GM. 2005. New approaches to nanofabrication: molding, printing, and other techniques. *Chem. Rev.* 105:1171–96

17. Barth JV, Costantini G, Kern K. 2005. Engineering atomic and molecular nanostructures on surfaces. *Nature* 437:671–79

18. Kushner DJ. 1969. Self-assembly of biological structures. *Bact. Rev.* 33:302–45

19. Klug A. 1983. From macromolecules to biological asssemblies (Nobel Lecture). *Angew. Chem. Int. Ed. Engl.* 22:565–82

20. Whitesides GM, Grzybowski B. 2002. Self-assembly at all scales. *Science* 295:2418–21

21. Kirschner M, Mitchison T. 1986. Beyond self-assembly: from microtubules to morphogenesis. *Cell* 45:329–42

22. Misteli T. 2001. The concept of self-organization in cellular architecture. *J. Cell Biol.* 155:181–85

23. John K, Bär M. 2005. Alternative mechanisms of structuring biomembranes: self-assembly versus self-organization. *Phys. Rev. Lett.* 95:198101

24. Ulman A. 1996. Formation and structure of self-assembled monolayers. *Chem. Rev.* 96:1533–54

25. Barth JV, Weckesser J, Lin N, Dmitriev S, Kern K. 2003. Supramolecular architectures and nanostructures at metal surfaces. *Appl. Phys. A* 76:645–52

26. De Feyter S, De Schryver FC. 2003. Two-dimensional supramolecular self-assembly probed by scanning tunneling microscopy. *Chem. Soc. Rev.* 32:139–50

27. Barlow SM, Raval R. 2003. Complex organic molecules at metal surfaces: bonding, organisation and chirality. *Surf. Sci. Rep.* 50:201–341

28. Nicolis G, Prigogine I. 1977. *Self-Organization in Nonequilibrium Systems: From Dissipative Structure Formation to Order Through Fluctuations*. New York: Wiley

29. Eigen M. 1971. Self-organization of matter and the evolution of biological macromolecules. *Naturwissenschaften* 33:465–523

30. Lehn JM. 2002. Toward self-organization and complex matter. *Science* 295:2400–3

31. Ertl G. 1991. Oscillatory kinetics and spatiotemporal self-organization in reactions at solid surfaces. *Science* 254:1750–55

32. Moison JM, Houzay F, Barthe F, Leprince L, André E, Vatel O. 1994. Self-organized growth of regular nanometer-scale InAs dots on GaAs. *Appl. Phys. Lett.* 64:196–98

33. Brune H, Giovannini M, Bromann K, Kern K. 1998. Self-organized growth of nanostructure arrays on strain-relief patterns. *Nature* 394:451–53

34. Cölfen H, Mann S. 2003. Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures. *Angew. Chem. Int. Ed. Engl.* 42:2350–65

35. Barth JV, Weckesser J, Cai C, Günter P, Bürgi L, et al. 2000. Building supramolecular nanostructures at surfaces by hydrogen bonding. *Angew. Chem. Int. Ed. Engl.* 39:1230–34

36. Rosei F, Schunack M, Naitoh Y, Jiang P, Gourdon A, et al. 2003. Properties of large organic molecules at surfaces. *Prog. Surf. Sci.* 71:95–146

37. Faul CFJ, Antonietti M. 2003. Ionic self-assembly: facile synthesis of supramolecular materials. *Adv. Mater.* 15:673–83

38. Nilsson A, Pettersson LGM. 2004. Chemical bonding on surfaces probed by X-ray emission spectroscopy and density functional theory. *Surf. Sci. Rep.* 55:49–167

39. Eremtchenko M, Schaefer JA, Tautz FS. 2003. Understanding and tuning the epitaxy of large aromatic adsorbates by molecular design. *Nature* 425:602–5

40. Fasel R, Wider J, Quitman C, Ernst KH, Greber T. 2004. Determination of the absolute chirality of adsorbed molecules. *Angew. Chem. Int. Ed. Engl.* 43:2853–56

41. Hauschild A, Karki K, Rowie BCC, Rohlfing M, Tautz FS, Sokolowski M. 2005. Molecular distortions and chemical bonding of a large π-conjugated molecule on a metal surface. *Phys. Rev. Lett.* 94:036106

42. Okuno Y, Yokoyama T, Yokoyama S, Kamikado T, Mashiko S. 2002. Theoretical study of benzonitrile clusters in the gas phase and their adsorption onto a Au(111) surface. *J. Am. Chem. Soc.* 124:7218–25

43. Vladimirova M, Trimarchi G, Baldereschi A, Weckesser J, Kern K, et al. 2004. Substrate-induced supramolecular ordering of functional molecules: theoretical modelling and STM investigation of the PEBA/Ag(111) system. *Acta Mater.* 52:1589–96

44. Preuss M, Schmidt WG, Bechstedt F. 2005. Coulombic amino group-metal bonding: adsorption of adenine on Cu(110). *Phys. Rev. Lett.* 94:236102

45. Alkauskas A, Baratoff A, Bruder C. 2006. Site-selective adsorption of naphthalene-tetracarboxylic dianhydride on Ag(110): first-principles calculations. *Phys. Rev. B* 73:165408

46. Dmitriev A, Lin N, Weckesser J, Barth JV, Kern K. 2002. Supramolecular assemblies of trimesic acid on a Cu(100) surface. *J. Phys. Chem. B* 106:6907–12

47. Marchenko O, Cousty J. 2000. Molecule length-induced reentrant self-organization of alkanes in monolayers adsorbed on Au(111). *Phys. Rev. Lett.* 84:5363–66

48. Thayer GE, Sadowski JT, Heringdorf FM, Sakurai T, Tromp RM. 2005. Role of surface electronic structure in thin film molecular ordering. *Phys. Rev. Lett.* 95:256106

49. Jung TA, Schlittler RR, Gimzewski JK. 1997. Conformational identification of individual adsorbed molecules with the STM. *Nature* 386:696–98

50. Yokoyama T, Yokoyama S, Kamikado T, Mashiko S. 2001. Nonplanar adsorption and orientational ordering of porphyrin molecules on Au(111). *J. Chem. Phys.* 115:3814–18

51. Gerlach A, Schreiber F, Sellner S, Dosch H, Vartanyants IA, et al. 2005. Adsorption-induced distortion of $F_{16}CuPc$ on Cu(111) and Ag(111): an X-ray standing wave study. *Phys. Rev. B* 71:205425

52. Auwärter W, Weber-Bargioni A, Schiffrin A, Riemann A, Barth JV. 2006. Self-assembly and conformation of tetrapyridyl-porphyrin on the Ag(111) surface. *J. Chem. Phys.* 124:194708

53. Weigelt S, Busse C, Petersen L, Rauls E, Hammer B, et al. 2005. Chiral switching by spontaneous conformational change in adsorbed organic molecules. *Nat. Mater.* 5:112–17

54. Mendoza SM, Whelan CM, Jalkanen JP, Zerbetto F, Gatti FG, et al. 2005. Experimental and theoretical study of the adsorption of fumaramide[2]rotaxane on Au(111) and Ag(111) surfaces. *J. Chem. Phys.* 123:244708

55. Klappenberger F, Cañas-Ventura ME, Schlickum U, Clair S, Pons S, et al. 2006. Conformational adaptation in the self-assembly of an oxalic amide derivate on Au(111). Submitted

56. Ernst KH. 2006. Supramolecular surface chirality. *Top. Curr. Chem.* 265:209–52

57. Schunack M, Petersen L, Kühnle A, Lægsgaard E, Steensgard L, et al. 2001. Anchoring of organic molecules to a metal surface: HtBDC on Cu(110). *Phys. Rev. Lett.* 86:456–59

58. Weckesser J, Barth JV, Kern K. 2001. Mobility and bonding transition of C_{60} on Pd(110). *Phys. Rev. B* 64:161404

59. Weckesser J, Cepek C, Fasel R, Barth JV, Baumberger F, et al. 2001. Binding and ordering of C_{60} on Pd(110): investigations at the local and mesoscopic scale. *J. Chem. Phys.* 115:9001–9

60. Langlais VA, Gauthier Y, Belkhir H, Maresca O. 2005. Self-organized calix[4]arenes on Au(110)-(1 × 2): a combined low-energy electron diffraction and scanning tunneling microscopy experimental study with molecular mechanics calculations. *Phys. Rev. B* 72:085444

61. Stengel M, De Vita A, Baldereschi A. 2005. Adatom-vacancy mechanisms for the C_{60}/Al(111)-(6 × 6) reconstruction. *Phys. Rev. Lett.* 91:166101

62. Böhringer M, Morgenstern K, Schneider WD, Berndt R, Mauri F, et al. 1999. Two-dimensional self-assembly of supramolecular clusters and chains. *Phys. Rev. Lett.* 83:324–27

63. Yokoyama T, Yokoyama S, Kamikado T, Okuno Y, Mashiko S. 2001. Selective assembly on a surface of supramolecular aggregates of controlled size and shape. *Nature* 413:619–21

64. Weckesser J, De Vita A, Barth JV, Cai C, Kern K. 2001. Mesoscopic correlation of supramolecular chirality in one-dimensional hydrogen-bonded assemblies. *Phys. Rev. Lett.* 87:096101

65. Yokoyama T, Kamikado T, Yokoyama S, Mashiko S. 2004. Conformation selective assembly of carboxyphenyl substituted porphyrins on Au(111). *J. Chem. Phys.* 121:11993–97

66. Otero R, Naitoh Y, Rosei F, Jiang P, Thostrup P, et al. 2004. One-dimensional assembly and selective orientation of lander molecules on an O-Cu template. *Angew. Chem. Int. Ed. Engl.* 43:2092–95

67. Barth JV. 2000. Transport of adsorbates at metal surfaces: from thermal migration to hot precursors. *Surf. Sci. Rep.* 40:75–150

68. Barth JV. 2006. Mobility of complex organic species at metal surfaces. In *Properties of Single Molecules on Crystal Surfaces*, ed. P Grütter, W Hofer, F Rosei, pp. 269–86. Singapore: World Sci.

69. Weckesser J, Barth JV, Kern K. 1999. Direct observation of surface diffusion of large organic molecules at metal surfaces: PVBA on Pd(110). *J. Chem. Phys.* 110:5351–54

70. Schunack M, Linderoth TR, Rosei F, Laegsgaard E, Stensgaard I, Besenbacher F. 2002. Long jumps in the surface diffusion of large molecules. *Phys. Rev. Lett.* 88:156102

71. Otero R, Hummelink F, Sato F, Legoas SB, Thostrup P, et al. 2004. Lock-and-key effect in the surface diffusion of large organic molecules probed by STM. *Nature Mater.* 3:779–82

72. Miwa JA, Weigelt S, Gersen H, Besenbacher F, Rosei F, Linderoth TR. 2006. Azobenzene on Cu(110): adsorption site-dependent diffusion. *J. Am. Chem. Soc.* 128:3164–65

73. Raut JS, Fichthorn KA. 1998. Diffusion mechanisms of short-chain alkanes on metal substrates. *J. Chem. Phys.* 108:1626–35

74. Kwon KY, Wong KL, Pawin G, Bartels L, Stolbov S, Rahman TS. 2005. Unidirectional adsorbate motion on a high-symmetry surface: "Walking" molecules can stay the course. *Phys. Rev. Lett.* 95:166101

75. Zambelli T, Lagoute J, Ojeda CJV, Coudret S, Gauthier S. 2006. Tailoring the mobility of a 3D molecule adsorbed on a metal surface. *J. Phys. Chem. B* 109:14266–69

76. Lauhon LJ, Ho W. 1999. Single molecule thermal rotation and diffusion: acetylene on Cu(001). *J. Chem. Phys.* 111:5633–36

77. Gimzewski JK, Joachim C, Schlittler RR, Langlais V, Tang H, Johannsen I. 1998. Rotation of a single molecule within a supramolecular bearing. *Science* 281:531–33

78. Lin N, Dmitriev A, Weckesser J, Barth JV, Kern K. 2002. Real-time single-molecule imaging of the formation and dynamics of coordination compounds. *Angew. Chem. Int. Ed. Engl.* 41:4779–83

79. Shirai Y, Osgood AJ, Zhao Y, Yao Y, Saudan L, et al. 2006. Surface-rolling molecules. *J. Am. Chem. Soc.* 128:4854–64

80. Kottas GS, Clarke LI, Horinek D, Michl J. 2005. Artificial molecular motors. *Chem. Rev.* 105:1281–376

81. Tsong TT. 1988. Experimental studies of the behavior of single adsorbed atoms on solid surfaces. *Rep. Prog. Phys.* 51:759–832

82. Merrick ML, Luo W, Fichthorn KA. 2003. Substrate-mediated interactions on solid surfaces: theory, experiment and consequences for thin film morphology. *Prog. Surf. Sci.* 72:117–34

83. Barth JV, Zambelli T, Wintterlin J, Schuster R, Ertl G. 1997. Direct observation of mobility and interactions of oxygen molecules chemisorbed on the Ag(110) surface. *Phys. Rev. B* 55:12902–905

84. Silly F, Pivetta M, Ternes M, Patthey F, Pelz JP, Schneider WD. 2004. Creation of an atomic superlattice by immersing metallic adatoms in a two-dimensional electron sea. *Phys. Rev. Lett.* 92:016101

85. Lukas S, Witte G, Wöll C. 2002. Novel mechanism for molecular self-assembly

on metal substrates: unidirectional rows of pentacene on Cu(110) produced by substrate-mediated repulsion. *Phys. Rev. Lett.* 88:028301

86. Sykes ECH, Han P, Kandel SA, Kelly KF, McCarty GS, Weiss PS. 2003. Substrate-mediated interactions and intermolecular forces between molecules adsorbed on surfaces. *Acc. Chem. Res.* 36:945–53

87. Barth JV, Weckesser J, Trimarchi G, Vladimirova M, De Vita A, et al. 2002. Stereochemical effects in supramolecular self-assembly at surfaces: 1-D vs 2-D enantiomorphic ordering for PVBA and PEBA on Ag(111). *J. Am. Chem. Soc.* 124:7991–8000

88. Schiffrin A, Riemann A, Auwärter W, Pennec Y, Weber-Bargioni A, et al. 2007. Zwitterionic self-assembly of *L*-methionine nanogratings on the Ag(111) surface. *Proc. Natl. Acad. Sci. USA.* In press

89. Pennec Y, Auwärter W, Schiffrin A, Weber-Bargioni A, Barth JV. 2007. Supramolecular gratings for tunable confinement of electrons on metal surfaces. *Nat. Nanotechnol.* 2:99–103

90. Barth JV, Brune H, Ertl G, Behm RJ. 1990. Scanning tunneling microscopy observations on the reconstructed Au(111) surface: atomic structure, long-range superstructure, rotational domains, and surface defects. *Phys. Rev. B* 42:9307–18

91. Kern K, Niehus H, Schatz A, Zeppenfeld P, George J, Comsa G. 1991. Long-range spatial self-organization in the adsorbate-induced restructuring of surfaces: Cu(110)-(2 × 1)O. *Phys. Rev. Lett.* 67:855–58

92. Kühnle A, Linderoth TR, Hammer B, Besenbacher F. 2002. Chiral recognition in dimerization of adsorbed cysteine observed by scanning tunneling microscopy. *Nature* 415:891–93

93. Kühnle A, Molina LM, Linderoth TR, Hammer B, Besenbacher F. 2004. Growth of unidirectional rows of cysteine on Au(110)-(1 × 2) driven by adsorbate-substrate interactions. *Phys. Rev. Lett.* 93:086101

94. Clair S, Pons S, Fabris S, Baroni S, Brune H, et al. 2006. Monitoring two-dimensional coordination reactions: directed assembly of Co-terephthalate nanosystems on Au(111). *J. Phys. Chem. B* 110:5627–32

95. Seitsonen AP, Lingenfelder M, Spillmann H, Dmitriev A, Stepanow S, et al. 2006. Density functional theory analysis of metallosupramolecular architecture at surfaces: the Fe-diterephthalate nanoarray on Cu(100). *J. Am. Chem. Soc.* 126:5634–35

96. Steiner T. 2002. The hydrogen bond in the solid state. *Angew. Chem. Int. Ed. Engl.* 41:48–76

97. Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. 2003. Reticular synthesis and the design of new materials. *Nature* 423:705–14

98. Kitagawa S, Kitaura R, Noro S. 2004. Functional coordination polymers. *Angew. Chem. Int. Ed. Engl.* 43:2334–75

99. Kawai T, Tanaka H, Nakagawa T. 1997. Low dimensional self-organization of DNA-base molecules on Cu(111) surfaces. *Surf. Sci.* 386:124–36

100. Furukawa M, Tanaka H, Kawai T. 2001. The role of dimer formation in the self-assemblies of DNA base molecules on Cu(111) surfaces: a scanning tunneling microscopy study. *J. Chem. Phys.* 115:3419–23

101. Chen Q, Richardson NV. 2003. Enantiomeric interactions between nucleic acid bases and amino acids on solid surfaces. *Nat. Mater.* 2:324–28

102. Furukawa M, Tanaka H, Sugiara K, Sakata Y, Kawai T. 2000. Fabrication of molecular alignment at the specific sites on Cu(111) surfaces using self-assembly phenomena. *Surf. Sci.* 445:L58–63

103. Kelly REA, Kantorovich LN. 2006. Planar nucleic acid base superstructures. *J. Mater. Chem.* 16:1894–905

104. Clair S, Pons S, Seitsonen AP, Brune H, Kern K, Barth JV. 2004. STM study of terephthalic acid self-assembly on Au(111): hydrogen-bonded sheets on an inhomogenous substrate. *J. Phys. Chem. B* 108:19392–97

105. Griessl S, Lackinger M, Edelwirth M, Hietschold M, Heckl WM. 2002. Self-assembled two-dimensional molecular host-guest architectures from trimesic acid. *Single Mol.* 3:25–31

106. Lin N, Payer D, Dmitriev A, Strunskus T, Wöll C, et al. 2005. Two-dimensional adatom gas bestowing dynamic heterogeneity on surfaces. *Angew. Chem. Int. Ed. Engl.* 44:1488–91

107. Kühnle A, Linderoth TR, Besenbacher F. 2003. Self-assembly of monodispersed, chiral nanoclusters of cysteine on the Au(110)-(1 × 2) surface. *J. Am. Chem. Soc.* 125:14680–81

108. Theobald JA, Oxtoby NS, Phillips MA, Champness NR, Beton PH. 2003. Controlling molecular deposition and layer structure with supramolecular surface assemblies. *Nature* 424:1029–31

109. Perdigão LMA, Perkins EW, Ma J, Staniec PA, Rogers BL, et al. 2006. Bimolecular networks and supramolecular traps on Au(111). *J. Phys. Chem. B* 110:12539–42

110. Hipps KW, Scudiero L, Barlow DE, Cooke MP. 2002. A self-organized 2-dimensional bifunctional structure formed by supramolecular design. *J. Am. Chem. Soc.* 124:2126–27

111. Gross L, Moresco F, Ruffieux P, Gourdon A, Joachim C, Rieder KH. 2005. Tailoring molecular self-organization by chemical synthesis: hexaphenylbenzene, hexa-*peri*-hexabenzocoronene, and derivatives on Cu(111). *Phys. Rev. B* 71:165428

112. Abel M, Oison V, Koudia M, Maurel C, Katan C, Porte L. 2006. Designing a new two-dimensional molecular layout by hydrogen bonding. *Chemphyschem* 7:82–85

113. Perdigão LMA, Champness NR, Beton PH. 2006. Surface self-assembly of the cyanuric acid–melamine hydrogen bonded network. *Chem. Comm.* 2006:538–40

114. Otero R, Schöck M, Molina LM, Laegsgaard E, Stensgaard I, et al. 2004. Guanine quartet networks stabilized by cooperative hydrogen bonds. *Angew. Chem. Int. Ed. Engl.* 44:2–6

115. Stepanow S, Lin N, Vidal F, Landa A, Ruben M, et al. 2005. Programming supramolecular assembly and chirality in dicarboxylate networks on a Cu(100) surface. *Nano Lett.* 5:901–4

116. Vidal F, Delvigne E, Stepanow S, Lin N, Barth JV, Kern K. 2005. Chiral phase transition in two-dimensional supramolecular assemblies of prochiral molecules. *J. Am. Chem. Soc.* 127:10101–6

117. Cañas-Ventura ME, Klappenberger F, Clair S, Pons S, Barth JV, et al. 2006. Coexistence of one- and two-dimensional supramolecular assemblies of terephthalic acid on Pd(111) due to self-limiting deprotonation. *J. Chem. Phys.* 125:184710

118. Payer D, Comisso A, Dmitriev A, Strunskus T, Lin N, et al. 2007. Ionic hydrogen bonds in 2-dimensional supramolecular systems at metal surfaces. *Chem. Eur. J.* In press

119. Stöhr M, Wahl M, Galka CH, Riehm T, Jung TA, Gade LH. 2005. Controlling molecular assembly in two dimensions: the concentration dependence of thermally induced 2D aggregation of molecules on a metal surface. *Angew. Chem. Int. Ed. Engl.* 44:7394–98

120. Griessl SJH, Lackinger M, Jamitzky F, Markert T, Hietschold M, Heckl WM. 2004. Room-temperature scanning tunneling microscopy manipulation of single C_{60} molecules at the liquid-solid interface: playing nanosoccer. *J. Phys. Chem. B* 108:11556–60

121. Wild M, Berner S, Suzuki H, Yanagi H, Schlettwein D, et al. 2002. A novel route to molecular self-assembly: self-intermixed monolayer phases. *Chemphyschem* 3:881–85

122. Xu B, Tao CG, Cullen WG, Reutt-Robey J, Williams ED. 2005. Chiral symmetry breaking in two-dimensional C_{60}-ACA intermixed systems. *Nano Lett.* 5:2207–11

123. Bonifazi D, Spillmann H, Kiebele A, Wild M, Seiler P, et al. 2004. Supramolecular patterned surfaces driven by cooperative self-assembly of C_{60} and porphyrins on metal substrates. *Angew. Chem. Int. Ed. Engl.* 43:4759–63

124. Spillmann H, Kiebele A, Jung TA, Bonifazi D, Cheng F, Diederich F. 2006. A two-dimensional porphyrin-based porous network featuring communicating cavities for the templated complexation of fullerenes. *Adv. Mater.* 18:275–79

125. Pan GB, Liu JM, Zhang HM, Wan LJ, Zheng QY, Bai CL. 2003. Configurations of a calix[8]arene and a C_{60}/calix[8]arene complex on a Au(111) surface. *Angew. Chem. Int. Ed. Engl.* 42:2747–51

126. Dmitriev A, Spillmann H, Lin N, Barth JV, Kern K. 2003. Modular assembly of two-dimensional metal-organic coordination networks at a metal surface. *Angew. Chem. Int. Ed. Engl.* 41:2670–73

127. Stepanow S, Lingenfelder M, Dmitriev A, Spillmann H, Delvigne E, et al. 2004. Steering molecular organization and host-guest interactions using tailor-made two-dimensional nanoporous coordination systems. *Nat. Mater.* 3:229–33

128. Auwärter W, Weber-Bargioni A, Klappenberger F, Schiffrin A, Barth JV, et al. 2006. Conformational adaptation and selective adatom capturing of tetrapyridyl-porphyrin molecules on Cu(III). Submitted

129. Auwärter W, Weber-Bargioni A, Brink S, Schiffrin A, Barth JV, et al. 2007. Controlled metalation of self-assembled porphyrin nanoarrays in two dimensions. *Chemphyschem* 8:250–54

130. Lingenfelder M, Spillmann H, Dmitriev A, Stepanow S, Lin N, et al. 2004. Towards surface-supported supramolecular architectures: tailored coordination assembly of 1,4-benzenedicarboxylate and Fe on Cu(100). *Chem. Eur. J.* 10:1913–19

131. Dmitriev A, Spillmann H, Lingenfelder M, Lin N, Barth JV, Kern K. 2004. Design of extended surface-supported chiral metal-organic arrays comprising mononuclear iron centers. *Langmuir* 41:4799–801

132. Messina P, Dmitriev A, Lin N, Spillmann H, Abel M, et al. 2002. Direct observation of chiral metal-organic complexes assembled on a Cu(100) surface. *J. Am. Chem. Soc.* 124:14000–1

133. Classen T, Fratesi G, Costantini G, Fabris S, Stadler FL, et al. 2005. Templated growth of metal-organic coordination chains at surfaces. *Angew. Chem. Int. Ed. Engl.* 44:6142–45

134. Lin N, Stepanow S, Vidal F, Barth JV, Kern K. 2005. Manipulating surface-supported diiron units via ligand control. *Chem. Comm.* 2005:1681–83

135. Schlickum U, Klappenberger F, Zoppelaro G, Ruben M, Barth JV, et al. 2006. Cobalt-directed assembly of ditopic cyanophenyl linker molecules to realize nanoporous metal-organic networks on Ag(111). Submitted

136. Clair S, Pons S, Brune H, Kern K, Barth JV. 2005. Mesoscopic metallo-supramolecular texturing through hierarchic assembly. *Angew. Chem. Int. Ed. Engl.* 44:7294–97

137. Gambardella P, Stepanow S, Dmitriev A, Gupta SS, Honolka J, et al. 2006. Tunable electronic and magnetic properties of Fe centers in a two-dimensional metallosupramolecular layer. Submitted

138. Blüm MC, Cavar E, Pivetta M, Patthey F, Schneider WD. 2005. Conservation of chirality in a hierarchical supramolecular self-assembled structure with pentagonal symmetry. *Angew. Chem. Int. Ed. Engl.* 44:5334–37

139. Spillmann H, Dmitriev A, Lin N, Messina P, Barth JV, Kern K. 2003. Hierarchical assembly of two-dimensional homochiral nanocavity arrays. *J. Am. Chem. Soc.* 125:10725–28

140. Blüm MC, Pivetta M, Patthey F, Schneider WD. 2006. Probing and locally modifying the intrinsic electronic structure and the conformation of supported nonplanar molecules. *Phys. Rev. B* 73:195409

141. Stepanow S, Lin N, Barth JV, Kern K. 2006. Binding of organic guests at two-dimensional metallosupramolecular hosts. *Chem. Comm.* 2006:2153–55

142. Newkome GR, Wang P, Moorefield CN, Cho TJ, Mohapatra PP, et al. 2006. Nanoassembly of a fractal polymer: a molecular "Sierpinski hexagonal gasket." *Science* 312:1782–85

143. Vonau F, Suhr D, Aubel D, Bouteiller L, Reiter G, Simon L. 2005. Evolution of multilevel order in supramolecular assemblies. *Phys. Rev. Lett.* 94:066103

144. Cañas-Ventura ME, Xiao W, Wasserfallen D, Barth JV, Fasel R, et al. 2007. Self-assembly of periodic bicomponent wires and ribbons. *Angew. Chem. Int. Ed. Engl.* 46:1814–18

145. Joachim C, Gimzewski JK, Aviram A. 2000. Electronics using hybrid-molecular and mono-molecular devices. *Nature* 408:541–48

146. Hagfeldt A, Grätzel M. 2000. Molecular photovoltaics. *Acc. Chem. Res.* 33:269–77

147. Seeman NC, Belcher AM. 2002. Emulating biology: building nanostructures from the bottom up. *Proc. Natl. Acad. Sci. USA* 99:6451–55

148. Whitesides GM. 2003. The 'right' size in nanobiotechnology. *Nat. Biotechnol.* 21:1161–65

149. Niemeyer CM. 2001. Nanoparticles, proteins and nucleic acids: Biotechnology meets materials science. *Angew. Chem. Int. Ed. Engl.* 40:4128–58

150. Balzani V, Credi A, Raymo FM, Stoddart JF. 2000. Artificial molecular machines. *Angew. Chem. Int. Ed. Engl.* 39:3348–91