Design and construction of on-surface molecular nanoarchitectures: lessons and trends from trimesic acid and other small carboxylyated building blocks

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Abstract

Molecular self-assembly and reactions at surfaces provide a versatile and appealing approach to nanomaterials synthesis, with a tremendous potential for engineering purpose-driven nanoarchitectures. However, since the outcomes of these processes depend on the chosen substrate, molecular constituents and processing conditions, the parameter space that must be mastered to control the product is enormous. Carboxylated molecules are a useful model system for illustrating the challenges and opportunities in creating on-surface nanoassemblies. These molecular building blocks can self-assemble through hydrogen bonding, or can deprotonate to enable ionic hydrogen bonds or organometallic bonding. Decarboxylation can lead to C–C bond formation and the on-surface synthesis of conjugated polymers. By focussing on key lessons from studies of carboxylated molecules, we highlight the challenges and opportunities in using these building blocks to form complex assemblies at the vanguard of materials design.

1. Introduction

The ability to facilitate and observe self-assembly on surfaces provides us with unparalleled insight into the behaviour of matter on the molecular scale [1]. Much of the progress in the field is due to the ability of scanning probe microscopy (SPM) to provide an atom-level view into molecules and their self-assembly processes [2]. Visualizing organization and pattern-
making on a molecule-by-molecule basis provides a means to directly reveal the behaviour of molecular systems, which can be taken as a microcosm of more general physics. For example, imaging of substrate-supported 2D molecular crystals can reveal whether they adhere to classical nucleation theory [3], and can demonstrate growth phenomena like Ostwald ripening [4].

Careful study of thin molecular films can provide insight into a range of topics. Molecular self-assembly is a core mechanism in biological systems [5]. For biological processes that normally evolve in 3D in solution, the reduced complexity associated with the two-dimensional constraint of a surface can allow 2D systems to stand as models that can help to reveal the subtle balance of interactions that lead to important outcomes. Examples include the information encoding associated with nucleic acid base pairing [6], or the polymerization mechanisms behind the formation of eumelanin [7], a biologically-significant pigment. Considerations of 2D self-assembly can also reveal how molecular interactions dictate the structure and function of organic semiconducting devices, where molecular geometry and crystallinity within the thin film can have a profound effect on the device properties [8]. Although studies of self-assembly can be used to elucidate complex 3D biological and thin film systems, much of the work in the field contributes to the overarching goal of achieving predictive control over the 2D self-assembly process, with an eye towards engineered materials [9]. The lowest-energy structure defined by molecular self-assembly at a surface depends on a range of parameters including the size and functionalization of the molecular building block(s), the substrate and the molecular coverage. In distinguishing between kinetic and thermodynamic structures, the processing conditions (temperature, deposition rate) are of paramount significance. For experiments conducted in solution, even more parameters must be considered, such as building block solubility, solvophobicity and solvent coadsorption. Amassing a library of experimentally-observed structures, and coupling it to calculations that reveal the energetics of the observed architectures, is of vital importance in our trajectory towards designing and realizing surface-supported self-assembled molecular systems that have been tailored for specific functionality.

Achieving predictive control over 2D self-assembly will enable the tailored design and synthesis of materials engineered for specific functionality (figure 1). Here, we focus on an important class of molecular building blocks: planar aromatic carboxylated molecules. These small molecules can be thought of as a model system for on-surface molecular nanoarchitectural design and realization. They have been extensively studied, and lessons learned from their behaviour can inform our understanding of other molecular systems. Furthermore, some of the most interesting emerging trends in surface-confined molecular materials have been demonstrated using carboxylated molecules.
In this review, we draw on selected works to demonstrate the versatility and applicability of molecular building blocks for addressing the challenge of designing and actualizing novel nanoscale assemblies. The focus here is on the behaviour of small carboxylated molecules on surfaces. The self-assembly of carboxylic acids at surfaces was reviewed a decade ago by Lackinger and Heckl [10]. Ivasenko and Perepichka looked at the parallels between 2D and 3D assembly of carboxylated molecules in 2011 [11], and in 2018 Lingenfelder and colleagues reviewed the formation of coordination networks from carboxylate groups [12]. The 2D self-assembly of telechelic carboxylated molecules has also recently been reviewed [13]. There have also been a number of general reviews of 2D self-assembly in recent years [14], as well as reviews covering more specialized cases like molecular assembly on 2D materials [15], bicomponent assemblies [16] and guest/host chemistry in 2D supramolecular systems [17]. Reactions of carboxylated molecules at surfaces have been included in a number of comprehensive reviews of strategies for on-surface synthesis of covalent architectures [18], as well as in the context of surface-confined coordination chemistry [19].

2. Overview of carboxylated molecule self-assembly and reactions at surfaces

2.1. Basic principles
In the context of molecular pattern-making, self-assembly refers to the spontaneous organization of molecular building blocks through non-covalent interactions [20]. This kind of supramolecular chemistry is just one manifestation of self-assembly, which as a general concept arises in physical systems across length scales, and can be defined as pre-existing components self-organizing, via a reversible process, into an ordered structure where the structure can be engineered through the design of the building blocks [21].

2.1.1. Hydrogen bonding.
For molecular self-assembly at surfaces, these non-covalent interactions can be programmed via functional groups. The most predictable results in 2D crystal engineering will tend to arise from strong, directional interactions like hydrogen bonds, which are electrostatic interactions between an electronegative atom and a hydrogen atom bonded to another electronegative atom.

An operational definition of hydrogen bonding was provided in 1990 by Margaret Etter, based on a comprehensive survey of bonding motifs present in solid-state data sets. Her definition emphasizes the organizational consequences of bonding: ‘A hydrogen bond is an interaction that directs the association of a covalently bound hydrogen atom with one or more other atoms, groups of atoms, or molecules into an aggregate structure that is sufficiently stable to make it convenient for the chemist to consider it as an independent chemical species [22]’. In her review, Etter highlights the use of hydrogen bonding as a driving force for pattern formation in organic crystals, foreshadowing the widespread use of hydrogen bonding in 2D crystal engineering, where bulk crystallographic studies can provide important insight and guidance [11].

Hydrogen bonds can reasonably be classified based on the bond energy, bond distances, or based on criteria of how the hydrogen-bonded systems behave, and thus the exact definitions of hydrogen bond strength tend to vary depending on the chosen classification scheme. However, in most cases, a O–H⋯O=C bond will be referred to as a ‘strong hydrogen bond’, similar to N–H⋯O=C or O–H⋯O-H bonds, which have typical strengths of 4–15 kcal/mol [23]. In contrast, weak bonds such as C–H⋯O typically have strengths of less than 4 kcal/mol, and very strong bonds, which tend to occur in charged complexes, typically have strengths from 15–40 kcal/mol [23]. Of particular relevance to carboxylated molecules is hydrogen bonding of the carboxylate ion (−COO−), which is associated with increased bond strength and decreased bond lengths, for example in COOH⋯COO− cyclic bonds [24].

The patterns derived from hydrogen bonding provide an elegant paradigm for defining bonding geometries. Considering that molecules can be conceived of as nodes, and the hydrogen bonds between them as linkers, Etter proposed that hydrogen bonding motifs could be represented using graph set notation [22]. Under this formalism, hydrogen-bonded networks are reduced to combinations of simple patterns, denoted as chains, (C), rings (R), intramolecular hydrogen-bonds (S) and other finite patterns (D) [25]. In graph set notation, hydrogen-bonded structures are defined using the notation $G(a)(n)$, where $G$ denotes one of the primary bonding motifs, $a$ the number of hydrogen bond acceptor groups, $d$ the number of hydrogen bond donor groups, and $n$ the total number of atoms involved. For example,
the −COOH dimer bond, which is stabilized by cyclic O−H...O=O=C bonds, is represented as $R_2^2(8)$ in this notation, and so on (figure 2).

**Figure 2.** Ring-based bonding motifs for prototypical carboxylated molecule benzoic acid, showing the corresponding graph set notation and with hydrogen bonds indicated by dashed lines. Carbon atoms are shown in grey, oxygen atoms in red, and hydrogen in white. Structures have been optimised using MM2 in Chem3D.

### 2.1.2. Substrates.

The substrate plays a critical set of roles in the on-surface assembly and reactions of molecules. In general, experiments and simulations are performed using atomically clean, flat and crystalline surfaces. This presents a range of benefits: the samples are easier to characterize with high-resolution microscopy, they are amenable to diffraction experiments, and they present a well-defined chemical and physical structure for spectroscopic probes. Standard substrates for self-assembly investigations include single crystal metals, highly-oriented pyrolitic graphite (HOPG) and graphene. However, we note that the finite size of the domain in these latter two substrates can have consequences for self-assembly: for example, the rotational disorder of the graphene domains in graphene/Pt(1 1 1) produces a variety of grain-boundary effects in adsorbed hydrogen-bonded molecular layers [26].

The crystallinity of the substrate can impose epitaxial constraints onto the tiling of a molecular layer. This lattice-matching occurs due to the preference of molecules for stable adsorption sites, constituting an energetic contribution that competes with intermolecular interactions that define the equilibrium spacings for isolated molecules. However, these equilibrium intermolecular spacings can be somewhat elastic. This can be demonstrated by considering −COOH cyclic dimers: gas-phase density functional theory (DFT) calculations at the ωB97X-D/6-31G(d,p) level suggest that stretching the dimer bond by 0.4 Å from equilibrium (1.627 Å) carries a penalty of less than 0.087 eV/molecule, which is less than 20% of
the calculated bond strength of 0.464 eV/molecule [27]. As expected, compression carries a higher penalty, with a 0.4 Å compression from equilibrium costing nearly 0.17 eV/molecule. Thus, for substrates that present a reasonable adsorption enthalpy for the molecules, small perturbations from the equilibrium hydrogen bond distance can be tolerated in the pursuit of periodic tiling on preferred lattice sites. This kind of variation in hydrogen bond length is seen, for example, in 1,4-benzenedicarboxylic acid (terephthalic acid, TPA, see figure 3) on Au(1 1 1), where crystalline molecular phases comprise hydrogen bonds that vary by up to 20% [28].

![Commonly-studied di- and tri-carboxlyated molecules.](image)

**Figure 3.** Commonly-studied di- and tri-carboxlyated molecules.

The magnitude of the molecule/substrate interaction depends on the substrate reactivity, which is defined by the electronic structure of the surface [29]. The surface electronic properties will determine whether a molecule physisorbs or chemisorbs, and if it chemisorbs, how strongly. The chemisorption interaction of the molecule with the surface can be associated with a range of effects: charge transfer to or from the surface, distortion of the molecular bonding geometry, and weakening of bonds within the molecule [30]. For transition metals, the reactivity of a surface can be predicted based on calculations or measurements of the electronic structure. The $d$-band model, proposed by Hammer and Nørskov, invokes the hybridization of molecular adsorbates with metal states to relate reactivity to the distance of the metal $d$-band centre of mass from the Fermi level [31]. Higher placement of the $d$-band centre relative to the Fermi level correlates with higher reactivities, as
hybridization with molecular states leads to emptying of the molecular antibonding states and higher adsorption energies. Hence, selection of a substrate can be used to encourage either (non-covalent) self-assembly, or to facilitate molecular reactions.

2.2. Preparation of samples
The preparation of 2D molecular layers on surfaces can be approached in a number of ways. Often, the choice of sample preparation conditions is a pragmatic one, based on the desired characterization techniques. For example, solution/solid microscopy, by definition, requires solution processing, and the use of vacuum instrumentation requires a dry sample. Ambient analysis techniques necessitate the use of an inert substrate, whereas vacuum analysis techniques permit the use of reactive surfaces.

For solution-based studies, where molecules are cast or deposited onto a surface through dip-coating, molecules must be solvated in a suitable solvent, such as methanol [32], toluene [33] or water [34]. The substrates for these studies need to be relatively non-reactive, and tend to be HOPG, graphene or Au(1 1 1), although Buck’s group has had a great deal of success with studies on underpotential deposited copper and silver surfaces on Au(1 1 1) (see section 5.1.2) [35–39]. For in situ studies at the solution/solid interface, the solvent must be slow to volatilize, so that the solution concentration remains relatively constant over the course of the experiment. Suitable examples and other useful parameters are provided in [10]. Deposition in vacuum can be accomplished using either a heated evaporation sources (e.g. a Knudsen cell), or a dosing line, depending on the vapour pressure of the molecules [40]. Reactive substrates can be prepared in vacuum by thermal annealing, or by noble gas ion sputtering [40], leaving the surface atomically clean and suitable for subsequent deposition of molecules.

2.3. Tools for studying surface-confined self-assemblies

2.3.1. Scanning probe microscopies (SPM).
Scanning probe microscopies (SPM), and in particular scanning tunnelling microscopy (STM), have been important driving forces behind the accelerating understanding of molecular architectures at surfaces. High-resolution STM imaging can provide a wealth of information about molecular adsorption on surfaces, furnishing insight into the intermolecular interactions, epitaxial alignment, and molecular adsorption geometry (although the latter can often be difficult to discern if the molecule is non-planar). STM can be deployed in vacuum, in ambient, or at the solution/solid interface [41], making it a versatile technique that can offer views into diverse assembly processes. In STM, an atomically-sharp metal tip is brought close (typically sub-nm range) to a surface, and the application of a bias voltage causes current to pass between tip and sample via quantum tunnelling [42]. Since the amount of current measured in STM depends on the tip-sample distance, monitoring the current while rastering the tip across the surface provides a way of mapping the surface topography. However, the current also...
depends on the local density of states (LDOS) of the sample, so can also be used to probe electronic properties. This is most commonly accomplished through scanning tunnelling spectroscopy (STS), which measures the electronic features in both filled and empty states near the Fermi level [42].

Atomic force microscopy (AFM) can similarly provide detailed information about molecular ordering at surfaces. Like STM, it can be used in vacuum, ambient or at the solution/solid interface, but in contrast to STM its mode of operation tends to change between these different environments. In AFM, a sharp tip mounted on the end of a cantilever is brought close enough to a surface to experience van der Waals forces [43]. These forces cause a deflection of the cantilever, and this deflection can be monitored to measure the tip-sample interaction as the tip is rastered across the surface. In practice, AFM is often used in an oscillating mode, where the cantilever is vibrated and the tip-surface interactions are measured via a change in the amplitude or phase of the vibrational response [44]. This type of measurement is frequently used in ambient or liquid conditions. Conversely, under vacuum conditions, excellent spatial resolution can be obtained by frequency modulation AFM [45], which routinely offers atomic resolution on surfaces, and which can be used to obtain resolution of individual bonds in molecular material with a suitably functionalized tip [46].

2.3.2. Photon-based spectroscopies.

Vibrational spectroscopies, such as Raman and infrared absorption spectroscopy, are photon in-photon out methods that can elucidate the functional groups and bonding geometries present in molecular systems [47]. Raman spectroscopy has also emerged as a standard characterisation technique for studying 2D materials, like graphene, and can be used to reveal electronic changes like doping [48].

Photoelectron spectroscopy (PES) is a photon in-electron out technique that can reveal the chemistry and electronic structure of the near-surface region of materials. Using x-rays as probe photons, x-ray photoelectron spectroscopy (XPS) liberates core electrons from atoms, and can provide both a quantitative assessment of stoichiometry as well as the oxidation state of the atoms present [49]. In studies of carboxylated molecules, measurements of the carbon 1s core level can be used to directly measure whether the −COOH groups are intact or deprotonated, or whether the molecule has decarboxylated, with O 1s providing redundant information. Figure 4 shows PES collected from isophthalic acid (IPA, figure 3), for which the binding energy assignments are well established in the literature [50]. Ultraviolet photoelectron spectroscopy (UPS) probes the valence band region, and can be used to extract the work function of the surface.
Figure 4. PES collected from C1s (a) and O1s (b) using synchrotron radiation after IPA is deposited onto Cu(1 1 1) and annealed. The loss of the −COOH-related spectral weight after annealing to 230 °C is apparent in both core levels, and corresponds to deprotonation of the molecule. Decarboxylation is also evident from the reduction of spectral intensity for −COO−. Experimental parameters are described in [158].

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy is a photon in technique that measures features in the x-ray absorption spectrum in the vicinity of an absorption edge. In the NEXAFS process, the absorbed photon liberates a core electron, which can then transition to the unoccupied states, providing a signature of those states [51]. This process is extremely sensitive to the bonding environment of the originating atom, so NEXAFS is often referred to as a fingerprinting technique. For molecular adsorbates, NEXAFS provides a unique advantage: according to the dipole transition rules that govern the process, the probability for interacting with molecular orbitals depends on the spatial disposition of the orbital and the polarization of the photon source with respect to that orbital. Therefore, by acquiring NEXAFS spectra using polarized light at various angles with respect to the surface, the orientation of molecular adsorbates on a surface can be determined.
2.3.3. Electron-based techniques.

A range of electron-in techniques are also commonly used to provide insight into surface-confined and nanoscale systems, but damage induced by the electron beam means that these techniques are typically not appropriate for small-molecule organic systems. Low-energy electron diffraction (LEED), which can be used to measure surface periodicities in crystalline materials [52], is a typical example of a technique has been documented to damage organic layers [53], although low-current operation like that enabled by the higher detection sensitivity of channeltrons employed in spot profile analysing (SPA-)LEED [54] can reduce this effect. Transmission electron microscopy (TEM) can provide atomic-resolution visualization of materials that can be suitably prepared, but is known to modify organic materials through bond-breaking following electron-nucleus interactions [55].

A less-common, but critically important electron-based technique is inverse photoemission spectroscopy (IPES), the complementary technique to UPS. In IPES, an electron couples to a sample and radiatively decays into an unoccupied state, emitting a photon [56]. If both the electron and photon energy are known, the binding energy of the final state can be determined through energy conservation. Ramping either the electron energy or the photon detection energy while monitoring photon intensity provides insight into the sample’s unoccupied states. The former approach is known as isochromat mode, and the latter as spectroscopic mode.

IPES is generally based on photon detection in the vacuum ultraviolet (VUV) range (\( h\nu \sim 10 \text{ eV} \) for isochromat mode with a typical Geiger–Muller detection setup [57]), which corresponds to electron injection at energies that are known to damage molecular materials [58]. Ironically, this makes IPES unsuitable for a range of applications that are critically important to the characterization of molecular materials, including the measurement of the LUMO position with an absolute energy reference and determination of the electron affinity, an important parameter for organic devices [58]. However, recently a modified implementation of IPES, based on the detection of near-UV photons (\( h\nu < 5 \text{ eV} \)), has been shown to significantly reduce the damage to molecular materials through the use of lower-energy electrons [59]. This paves the way for a number of interesting studies of organic materials, and in particular for work where combined UPS/IPES measurements will allow for development and optimization of 2D organic layers for electronic modifications at surfaces.

2.3.4. Computational approaches.

Computational examinations of 2D molecular layers investigate the structures formed and their energetics, with the aim of identifying stable structures and providing insight into their formation. A frequently-used approach is DFT, which approximates the solution to the many-body problem of interacting electrons in a static potential with non-interacting electrons [60]. This computational method can determine lowest-energy geometries for isolated molecular species, gas-phase associations (bond enthalpies) and for surface-adsorbed layers, and is often
used, e.g. to determine the most probable geometry based on crystallographic unit cells or observations from SPM.

The time evolution of molecular systems can be examined with molecular dynamics or Monte Carlo methods. Molecular dynamics tends to be useful for systems of a few hundred atoms, with time scales of a few picoseconds, whereas Kinetic Monte Carlo simulations can handle more atoms and longer time scales [61]. In the case of molecular dynamics, the system evolves according to the specified potentials governing the interactions between atoms, meaning that the choice of interatomic potential is critical. For Monte Carlo simulations, an understanding of the rates of different activated processes is required. These can be accessed through DFT, experimental measurements or molecular dynamics.

3. Fundamental explorations in hydrogen-bond driven molecular self-assembly: trimesic acid as a model system

3.1. TMA self-assembly

The small, C$_{3h}$-symmetric molecule trimesic acid (TMA, figure 3) is a model system for the self-assembly of molecules on surfaces, and amply demonstrates the rich insight provided by studies of molecular self-assembly at surfaces.

3.1.1. TMA chicken wire structure.

The surface-confined self-assembly of TMA was first investigated through near-simultaneous works describing the evaporation of the molecule onto two different surfaces UHV [62, 63]. In experiments on HOPG, Griessl et al used STM to identify two porous polymorphs, which they termed as the chicken wire structure (figure 5(a)) and the flower structure (figure 5(b)), in which the molecules are stabilized by dimeric −COOH bonding and a combination of dimeric and trimeric TMA bonding, respectively. They noted that the ~1 nm pores defined within each of the architectures could host additional TMA molecules as guests. Later work used DFT to demonstrate that the TMA guests are most stable when adsorbed off centre in the pore, with guest molecules interacting with two −COOH dimer bonds [64]. In experiments on Cu(1 0 0), Dmitriev et al showed that deposition of TMA onto a surface cooled to −30 °C produced small (~20 nm × 20 nm) islands of TMA that primarily exhibited a chicken wire-like dimer-bonded motif [63]. Warming the surface to RT completely changed the molecular assembly, which evolved to a linear pattern of upright molecules, which the authors interpreted as arising from deprotonation and subsequent carboxylate interaction with the underlying copper surface. Only a few months later a porous array of TMA that comprised some chicken wire-like pores was reported to form on Au(1 1 1) under electrochemical conditions in 0.1 M HClO$_4$ containing 0.1 mM TMA at low potential ($E_s = +0.2$ V) [65].
The ubiquity of the dimer-bonding motif even under different processing conditions speaks to its robustness, which is further emphasized by the fact that the same dimer-bonded pores had been identified decades prior within the bulk TMA crystal structure [67]. This primary bonding motif of TMA, based on dimeric association into the chicken wire network, has been observed to assert under a range of conditions. In addition to those already mentioned, these include: at the 1-octanoic acid/bi- and tri-layer graphene on SiO$_2$ interfaces [68], the heptanoic acid/graphene on Cu interface [69], the phenyloctane/HOPG interface [70], in dried films on HOPG following deposition from solution in methanol [32] or water [71], under electrochemical conditions on Au(1 1 1) in 0.05 M H$_2$SO$_4$ [72], following vacuum deposition onto graphene/TEM grids and graphene on Cu [73], in UHV on Au(1 1 1) at 4.5 K [74], and at room temperature on Ag(1 1 1) [75, 76] and Cu(1 1 1) [75], as well as on Si(1 1 1)-(√3 × √3) [77].

Despite this extensive body of work on TMA chicken wire, there are still some outstanding questions, even regarding assembly on the most commonly-studied surface of HOPG. One particular question is around epitaxy. Observations based on FFT analyses of STM data have suggested that the TMA chicken wire lattice has its unit vectors oriented at a ~5° angle to the underlying HOPG lattice [63]. Half-and-half STM images showing both the HOPG atomic lattice and the TMA molecular lattice can be autocorrelated to extract the epitaxy matrix [69] which describes a TMA lattice rotated by ~7.5° with respect to the underlying HOPG, and with a lattice constant of $\sqrt{43}$ the HOPG lattice. This corresponds to a TMA lattice where the −COOH dimer bonds are compressed by ~0.4 nm from their gas-phase equilibrium length [69, 78]. The autocorrelation analysis does not allow identification of the adsorption sites associated with the TMA layer, but single-molecule DFT calculations have been used to investigate TMA adsorption of various HOPG high-symmetry sites [69]. Tersoff-Hamman simulated images show that adsorption on the lowest-energy sites leads to the characteristic inequivalent contrast (bright/dark) of the two three-molecule sublattices of TMA within the chicken wire pore often seen in STM images (as explicitly described in [69], and evident in other published works, e.g. figure 5(a) of [10]).
However, strong evidence for non-epitaxial adsorption also exists. Non-epitaxial adsorption leads to the formation of moiré patterns, which are interference phenomena arising from the rotation of one periodic lattice with respect to another, and which manifest as superlattice contrast modulations in STM images. The lack of epitaxy could arise if strict epitaxy does not provide large energetic gains relative to non-epitaxial adsorption, which is a plausible scenario for TMA on HOPG. The adsorption landscape for TMA on the HOPG surface has been calculated to be rather homogenous, without a large energy difference between high-symmetry sites [69], or even across theoretical adsorption trajectories comprising sites that are not well-defined. In TMA chicken wire layers, characteristic hexagonal superlattice patterns with moiré periodicities of with ~6 nm [79] and ~10 nm periodicity [80] had already been reported when moiré superstructures with a 5.85 ± 0.10 nm were the explicit focus of a work by Li et al in 2007 [81]. Recently, Lackinger’s group published work examining in detail the moiré patterns formed by TMA on HOPG which demonstrated that a range of moiré periodicities are possible [78]. This work showed that even with deposition of TMA solution onto a hot (100 °C) substrate, the tell-tale moiré patterns associated with non-epitaxial interactions could not be eliminated. In contrast, the work presented by Li et al reported that moiré patterns were removed through application of −4000 V to the TMA-covered graphite substrate for 90 min. They attribute this effect to reduced charge transfer enabling diffusion and allowing adsorption on the lowest energy sites [81].

One of the main findings of Lackinger’s recent work on moiré patterns is that all observed patterns can be explained by a TMA lattice with a fixed lattice parameter of $a_{TMA} = (1.652 ± 0.002)$ nm [78]. In other work, selected area electron diffraction (SAED) data collected using TEM through TMA chicken wire films 2.1 ± 0.2 nm and 5.5 ± 0.2 nm thick grown on graphene-covered TEM grids led to a measured periodicity of 1.64 ± 0.02 nm [78]. The small specified uncertainty range on this measurement makes it incompatible with the previously-quoted epitaxy matrix, but consistent with an uncompressed TMA lattice and with Lackinger’s proposed fixed lattice parameter [78].

The adsorption geometry of TMA on HOPG is thus an interesting and active research area, where continued efforts to study monolayers and thin films may reveal more about the rich behaviour of this system.

### 3.1.2. Other polymorphs.

Soon after the initial reports of TMA chicken wire formation under UHV and electrochemical conditions, subsequent work revealed that TMA self-assemblies could be fostered at the solution/solid interface. The chicken wire structure was shown to spontaneously form at the HOPG surface from solution in heptanoic acid [79, 82]. Heptanoic acid is an alkanoic acid, which are of the type defined by the general formula $C_nH_{2n+1}COOH$. In exploring the effects of different alkanoic acid solvents, Lackinger et al discovered that choice of solvent turns out to be critical to the TMA polymorph formed: from saturated solutions in nonanoic (C$_9$H$_{17}$COOH) and
octanoic (C\textsubscript{7}H\textsubscript{15}COOH) acids, TMA forms only chicken wire at the solution/HOPG interface, whereas from saturated solutions in butyric (C\textsubscript{2}H\textsubscript{2}COOH), pentanoic (C\textsubscript{3}H\textsubscript{4}COOH) and hexanoic (C\textsubscript{4}H\textsubscript{11}COOH) acids, TMA forms exclusively the flower structure [66]. In heptanoic acid (C\textsubscript{5}H\textsubscript{13}COOH), both polymorphs were observed to coexist. It is in this manuscript that the authors hypothesize that a fully-trimeric polymorph, which they term ‘superflower’ should also exist, although they had not observed it. In our work focusing on the co-assembly of TMA with linear carboxylated molecules, we found that domain boundaries could stabilize small regions of superflower, as well as other higher-order flower structures, implying that the TMA chicken wire and flower structures were sequential members of a homology of polymorphs extending from all-dimeric chicken wire to all-trimeric superflower [83].

However, it was a UHV study on Au(1 1 1) that unambiguously revealed a series of polymorphs that demonstrated this trend, showing how successively higher surface densities could be used to facilitate the formation of higher and higher order homologues, with larger and larger trimeric regions linked by dimeric domain boundaries connecting chicken wire pores (figure 6) [84]. According to the authors, each homologue represents a maximization of dimer bonds for a given coverage. Based on gas-phase DFT (B3LYP/6-31G(d,g)), we can consider whether the flower structure should be more stable than chicken wire. The calculated unit vector magnitudes are 1.66 nm and 2.63 nm (reported in [83]) for chicken wire and flower, respectively. The per-molecule bond enthalpies are −10.01 kcal/mol and −8.78 kcal/mol (reported in [85]), for dimeric and trimeric TMA bonding, respectively. Taken together with the bonding geometry of the molecules shown in figure 5, these numbers suggest that the chicken wire structure has a gas-phase areal enthalpy of −25.2 kcal/mol/nm\textsuperscript{2}, versus the flower structure value of −28.8 kcal/mol/nm\textsuperscript{2}, suggesting that the flower structure should be more stable. In on-surface adsorption, the molecule/substrate interactions would further favour flower structure, since it has a higher packing density than chicken wire. However, the details of this adsorption enthalpy are site-specific, and cannot be determined exactly without a full model for adsorption.
The concentration of molecules is also found to correlate with polymorph in solution/solid work, where the higher-density flower structure is formed from high-concentration solutions, and the lower-density chicken wire structure from lower-concentration solutions [83]. This empirical observation has been borne out by statistical thermodynamic modelling that shows that chicken wire then flower then superflower polymorphs are stabilized at increasing concentrations at room temperature [86]. However, a range of other solvent-related effects (the size of aggregates in solution, the deposition rate, solvent dielectric constant, etc) [10] may also influence polymorph selection in solution.

Solvophobicity can further influence TMA polymorph selection. TMA is relatively insoluble in phenyloctane, with a concentration too low to facilitate monolayer formation at the phenyloctane/HOPG interface [87]. Increasing the concentration through sonication results in solutions to facilitate the formation of a zigzag row polymorph that is not observed with other solvents. Ha et al interpret this densely-packed (1.29 ± 0.02 molecules nm$^{-2}$) zigzag phase as resulting from solvophobic effects: either from a thermodynamic preference driven by poor solubility, or from a kinetic trapping due to the inability of adsorbed molecules to dynamically re-exchange back to solution, with the preference for this polymorph instead of, e.g. superflower structure (theoretical density 1.19 molecules nm$^{-2}$), driven by its very high packing.

Figure 6. The homology of TMA polymorphs formed on Au(1 1 1). A–I show successively higher-order polymorphs that correspond to the models in a–i, with A/a showing the fully-dimeric chicken wire phase, and I/i showing the fully-trimeric superflower phase. STM images are 16.5 × 16.5 nm$^2$. Reprinted with permission from [84]. Copyright (2007) American Chemical Society.
density [87]. In a follow-up work, the same group extended this study of TMA solutions by showing that, for a given solvent, TMA concentration increases monotonically with sonication time. This allowed the team to show that the non-polar solvent phenyloctane only produces the zigzag structure, regardless of TMA concentration, whereas for the most strongly polar solvent tested, undecanol, the solvent co-assembled with the TMA at all concentrations, forming a lamellar structure previously-observed for coadsorption of TMA with alcohols (see section 3.2) [34, 88]. In the moderately polar solvent octanoic acid, concentration-dependent polymorphs were produced in the following order with increasing concentration: chicken wire → chicken wire with TMA-populated pores → flower → flower with TMA-populated pores [89]. The same progression from low to high density polymorphs can also be observed by modifying the temperature of the HOPG substrate from 20 °C to 80 °C during scanning [70].

Finally, we note that solution-based approaches to producing dried monolayer films also provide insight into how processing conditions can influence the polymorph formed. For example, drop-deposition of TMA from solution in methanol, a rapidly-evaporating solvent, leads to the same zig-zag phase polymorph produced through solvophobic effects in octadecanol [87, 89]. The drop deposition leads to zig-zag TMA in regions of the HOPG surface where step edges create densely-packed domains of the molecule [32]. Conversely, the same preparation procedure leads to chicken wire domains on open terraces, leading the authors to interpret the zigzag phase as being kinetically trapped due to high local molecular densities. Dried films can also be made directly from monolayers formed at the solution/HOPG interface by rinsing the droplet-covered substrate in water and then letting the sample dry [34]. TMA/graphene on Cu monolayers that exhibited the chicken wire phase at the heptanoic acid/solid interface revealed the flower structure following rinsing and drying [69]. Although the mechanism for this was not examined in detail, it could be due to the retention of some solution after rinsing, which would increase the concentration of TMA at the surface and perhaps drive the polymorph towards the denser-packed flower structure.

3.2. Co-crystals

In addition to reliably self-assembling on its own, TMA is amenable to a range of co-crystallizations with other molecules. This allows the possibility of, for example, using a similar threefold-symmetric −COOH hydrogen bonding molecule to modulate the size of the pores through co-crystallization, or using a linear molecule to reduce the symmetry of the molecular overlayer structure.

When combined in solution with 1,3,5-benzenetribenzoic acid (BTB), a molecule functionally identically to TMA but larger (0.9 nm diameter in TMA versus 1.8 nm diameter in BTB), the two species co-assemble into well-defined 2D networks at the solution/HOPG interface [90]. Varying the relative concentrations of TMA and BTB in heptanoic acid solution allows access to six different polymorphs, with TMA-dominant solutions producing typical TMA flower and chicken wire structures, and with dilute or BTB-dominant solutions leading to the formation of
TMA/BTB co-crystals or pure-BTB domains. Along with the expected TMA- and BTB-based chicken wire pores, with measured unit cell parameters of $a = b = 1.7$ nm for TMA and $a = b = 3.2$ nm for BTB, the co-crystalline polymorphs incorporated lower-symmetry pores bounded by combinations of TMA and BTB molecules. The authors of this work were able to reproduce the concentration-space phase diagram of the polymorphs through a model based on adsorption enthalpy and the concentration-dependent chemical potential of the molecules, demonstrating that the co-crystallization is predictable and thermodynamically stable.

Ordered chicken wire co-crystals can also form from molecules from $C_3$-symmetric molecules without −COOH functionalization when mixed with TMA. 1,3,5-tris(4-pyridyl)-2,4,6-triazine (TPT) fails to self-assemble on its own at the heptanoic acid/HOPG interface, but forms a chicken wire-like network in a 1:1 ratio with TMA at the HOPG interface with a binary solution of both molecules [91]. The pores, stabilized by N⋯H–O hydrogen-bonds, are larger than the TMA chicken wire pores because of the larger scaffold provided by the TPT, and the structure has a correspondingly larger unit cell parameter of $a = b \approx 2.0$ nm. The solution concentration was critical to the formation of this lattice, both in absolute concentration and in relative concentration of TMA:TPT—the TPT needed to be well in excess of the TMA (6:1 ratio) to prevent TMA–TMA −COOH bonding from dominating, and the absolute concentration needed to be low to prevent precipitation of bulk crystals.

Besides forming these structurally well-defined crystals, another possibility has been recently demonstrated: TMA can form a $R_5^2(8)$ hydrogen-bond-stabilized solid solution with terthienobenzenetricarboxylic acid (TTBTA, figure 3) at the heptanoic acid/HOPG interface [27]. This 2D system is an entropically-driven random alloy, where the larger TTBTA molecule substitutes into the TMA chicken wire lattice at about a rate of 1:10. This locally distorts the lattice, and leads to a larger average lattice constant for the intermixed lattice ($a = b = 1.7$ nm), which in turn is associated with a unique epitaxial arrangement, distinct from both pure TMA ($a = b = 1.61$ nm) and pure TTBTA lattices ($a = b = 2.37$ nm), on HOPG. Considerations of the Gibbs free energy of intermixing suggest that this intermixed lattice is thermodynamically stable because of the configurational entropy associated with the random intermixing; in absolute terms, the lattice energetics must be competitive (i.e. within $\sim kT$) with both the pure TMA and TTBTA lattices, since the intermixed domains coexist with these pure-phase lattices.

Inclusion of a second molecule within the molecular monolayer can also provide a means to change the symmetry of the assembly. For example, at the toluene/HOPG interface, a bimolecular solution of TMA with 4,4’-bipyridine (Bpy) forms a densely-packed linear structure comprising TMA-Bpy-TMA units with the network hypothesized to be driven by strong N⋯H–O interactions between TMA and Bpy while comprising relatively weak hydrogen bonds between TMA molecules (i.e. without $R_5^2(8)$ motifs) [92]. In UHV studies on Au(1 1 1), TMA was shown to co-assemble with 4,4’-bis(4-pyridyl)biphenyl into checkerboard motifs whose pore sizes and shapes could be modified through the ratio of the two molecules [93]. The rich
variety of accessible phases arises due to the range of hierarchical hydrogen bonding interactions facilitated by the building blocks, with seven identified bonding geometries arising the structures.

The co-assembly of TMA with linear alcohols (general formula C\textsubscript{n}H\textsubscript{2n+1}OH) produces a lamellar phase of alternating TMA dimers and interdigitated alcohols \cite{88}. The structure is stabilized by –COOH hydrogen bonding within the TMA dimer, C–O…H and C=O…H bonding between the alcohol –OH group and two adjacent TMA molecules in the dimer row, and vdW intermolecular and molecule-substrate interactions between the interdigitated alkyl chains \cite{34}. These latter interactions are maximized through an odd-even effect that manifests in different alkyl chain orientations with respect to the TMA dimer lamella (tilted by ~65° for even-parity alcohols versus perpendicular for odd-parity alcohols). Together with the selection of alcohol molecule length, this odd-even effect leads to a rational control over the spacing of the TMA dimer lamellae on the surface, providing an example of how a bicomponent molecular nanopattern can be designed and implemented.

### 3.3. Host-guest systems

At the solution/solid interface, suitable guest molecules can be easily introduced into the porous TMA network from solution, and specific focus has been given to highly-symmetric guest molecules that do not self-assemble at the solution/solid interface in the absence of a host template. In early work, both coronene \cite{79} and C\textsubscript{60} fullerene \cite{82} (figure 7) were shown to be amenable guests, with each of these molecules making a good geometric fit in the TMA pores, which allow access to the substrate for stabilization through adsorption interactions with the underlying HOPG. TMA can also be used to trap more exotic molecules, such as the circulenes known as sulflower and selenosulflower, which are size-matched to the TMA chicken wire pores \cite{94}. These planar molecules were found to aggregate into 3D assemblies from the TMA lattice, which shows that host/guest templating can be useful tool for nucleating thin-film crystal phases at the solution/solid interface.

![Figure 7. Common guest molecules for host/guest investigations.](image)

Planar circulene molecules like coronene, sulflower and selenosulflower have a distinct advantage as guests within a TMA structure: since they are approximately the same size and shape as the TMA chicken wire pore, the host-guest structure has areal-optimized molecule-substrate interactions and optimized host/guest interactions while at the same time retaining
the strong dimer-bonding motif within the TMA lattice. The stability of the TMA/coronene host/guest lattice was nicely illustrated through a set of experiments by Li et al that showed that bimolecular open lattices comprising TMA and a second bonding unit (either Bpy or 1,3,5-tris(4-pyridyl)-2,4,6-triazine, known as TPTZ) were quickly converted to chicken wire TMA/coronene host/guest lattices with the addition of coronene at the heptaonic acid/HOPG interface [95]. The authors present DFT calculations to support the interpretation of this phenomenon as thermodynamically driven, showing that the enthalpy of the TMA/coronene network exceeds that of the binary porous networks, even if the coronene/HOPG interaction is neglected. This clearly shows the stability of the size-matched host/guest lattices, and also demonstrates the possibility for using TMA as a responsive layer; this is further discussed in the next section.

Host-guest structures can also be useful in stabilizing bulkier molecules. González et al recently investigated the use of TMA chicken wire as a host for ‘Saturn-like’ macrocyclic oligothiophenes (figure 8(a)) complexed with fullerenes into a donor–acceptor complex [96]. These bulky molecules are too large to pack into every pore of the chicken wire structure, but define a crystalline lattice with a periodicity $\sqrt{3}$ times larger than the chicken wire lattice at the heptanoic acid/HOPG interface. The templated first-layer growth acts as a foundation for out-of-plane crystallization of a second layer, and STS measurements show that these bilayers exhibit rectifying behaviour.

**Figure 8.** (a) A Saturn-like oligothiophene-fullerene complex that templates into the TMA chicken wire structure at the heptanoic acid/HOPG interface. (b) The structural model for the packing observed in STM images. (c) STM image of the host/guest structure. Reproduced from [96]. CC BY 4.0.

### 3.3.1. Responsive TMA layers.
The response to external stimulus demonstrated by the bicomponent TMA networks in the previous section illustrates the possibility for TMA layers to be used as 'smart' materials whose properties can be switched in response to an environmental change. While the detection of an analyte (coronene) added to solution certainly constitutes a sensor-like response, the return to the original state (porous bicomponent networks) is thermodynamically disfavoured. Hence there are a range of applications where response to an externally switchable perturbation is useful, especially if toggling between states is possible through reversal of the perturbation. This has been demonstrated, e.g. by Gutzler et al's demonstration of the temperature-induced transition between BTB chicken wire structure and a densely-packed polymorph at the solution/solid interface [97]. Recent examples have also shown that TMA networks at the solution/solid interface can exhibit this sort of response to applied electric fields, which have the possibility to be more rapidly switched than thermal perturbations.

Zheng et al showed that with the application of a localized electric field (10^5 V m⁻¹, applied via the STM tip bias), an existing TMA chicken wire lattice could be transformed through the addition of second-layer 1,3,6,8-tetrakis(1-butyl-1H-1,2,3-triazol-4-yl)pyrene (TP) molecules from a binary solution of TMA and TP at the octanoic acid/HOPG interface [98]. By reversing the field direction, the bilayer structure of TP/TMA was transformed into a monolayer kagomé structure with a different periodicity and appearance in STM images. The authors propose that the bilayer structure results from protonation of the TP that makes the charged molecules sensitive to the applied field, favouring the bilayer structure under a positive field, and favouring the kagomé structure under all other conditions (negative or no applied field). The same mechanisms were tentatively proposed by Velpula et al to explain the local field-induced polymorph switching in BTB/TMA coassemblies and BTB/TMA/coronene guest-host networks at the heptanoic acid/HOPG interface [99].

The bias associated with the STM tip has also been used to modify the polymorph formed from TMA alone at the heptanoic acid/HOPG interface. Ubink et al showed that the TMA chicken wire structure could be switched to the flower structure by switching the STM bias polarity from negative to positive at the nonanoic acid/HOPG interface [100]. According to a rationale similar to that provided for TP/TMA, the authors suggest that the chicken wire/flower transformation is driven by electrostatics, with the slight negative charge of the carboxyl groups disfavouring high-density TMA adsorption when the sample is negatively biased. This work illustrates a general phenomenon of field-induced transformation of assemblies of carboxylated molecules, which was first observed for BTB at the nonanoic acid/HOPG interface, where switching between positive and negative bias polarities enabled a reversible switch between the chicken wire structure and a dimer phase [101]. The same authors, Cormetto et al, later showed that a similar bias-dependent polymorphism could be observed in a binary system of BTB with 4,4′-bis(4-pyridyl)terphenyl (BPTB) [102]. In this, the two molecular constituents add complexity to the system, whose observed structure depends on both relative concentration and bias voltage.
3.3.2. TMA as a model system—relation to self-assembly of other tricarboxylated molecules.

TMA has received a great deal of attention as a model system for 2D hydrogen bonding. It is useful to briefly look at how understanding developed based on studies of TMA can be extended to other molecular building blocks, and to consider the important ways in which other molecules deviate from behaviour demonstrated by TMA.

TMA sets a lower limit on the size of tri-carboxylated planar building blocks for molecular self assembly, and sets of baseline of behaviour for a high-symmetry molecule. Therefore, it is instructive to compare the behaviour of TMA to molecules that are larger and/or have lower symmetry.

BTB, which has been discussed previously in the context of bimolecular cocrystals, is a TMA analogue with a larger organic scaffold but identical symmetry. Studies of the self-assembly of BTB are therefore useful to examine how molecular size influences self-assembly. One consequence of BTB’s larger molecular scaffold is the possibility for the formation of O⋯H–C hydrogen bonds, which are not accessible for the smaller TMA molecules. These weaker hydrogen bonds have the enthalpic benefit of increasing molecular packing density, while at the same time leaving the polar –COOH groups available for interaction. Work from Kampschulte et al showed that, like TMA, BTB can form solvent-dependent polymorphs at the solution/solid interface [103]. However, in contrast to TMA, the bonding geometries of BTB are not solely driven by –COOH interactions; in addition to a -driven chicken wire phase, BTB forms an oblique phase stabilised through a combination of bonding (one bond per molecule) and two weaker O ⋯H–C interactions. This produces a denser packing than chicken wire, and asserts in more polar solvents, suggesting that solvent interactions with the exposed polar groups may help stabilize the structure.

These weak O⋯H–C interactions were found to dominate the self-assembly of the larger molecule 1,3,5-tris[40-carboxy-(1,10-biphenyl-4-yl)]benzene (TCBPB) at the solution/HOPG interface. TCBPB forms three distinct polymorphs, each of which incorporates the weak O⋯H–C bonding motif, including two BTB-like oblique phases and a porous chicken wire phase stabilized entirely by offset O⋯H–C bonds rather than dimer bonds [104]. Thermodynamic considerations suggest that this chiral offset chicken wire network is more stable than its dimer-bonded counterpart due to the denser packing and concomitant higher adsorption enthalpy afforded by the weaker O⋯H–C bonds.

The low-symmetry molecule biphenyl-3,4′,5-tricarboxylic acid (H3BHTC, figure 3) provides a unique opportunity to investigate how a molecule with both TMA-like and BTB-like substituents behaves. We found that in a saturated H3BHTC solution at the heptanoic acid/HOPG interface, the observed polymorph comprises strong –COOH dimer bonding along its short (TMA-like) axis, but weaker offset O⋯H–C bonding along its long (BTB-like) axis [105]. The overall effect is to create a moderately porous structure that is likely further stabilized
through solvent coadsorption within its cavities. The addition of coronene to the solution transforms the lattice to a higher-symmetry, fully-porous network that hosts coronene within two different pore types: a TMA chicken wire-like pore bounded by the short axes of six H3BHTC molecules, and slightly rectangular pores bounded by the long axes of four H3BHTC molecules. A later Monte Carlo study emphasized the stability of the TMA/coronene pores, and suggest that the modification to the H3BHTC structure likely nucleates through the formation of TMA/coronene pores [106], while an experimental study found that H2BHTC may also form phases with solvent coadsorption, particularly in longer-chain solvents like nonanoic acid [107].

The propensity for bonding can be built into the molecule building blocks by eliminating the benzoic acid-like configuration (para-bonded −COOH groups) that occurs in H3BHTC and BTB, and which fosters the weak O⋯H–C bonding. Structurally forcing the strong dimer bond can have interesting implications for the regularity of the resulting network. For example, p-terphenyl-3,5,3',5'-tetracarboxylic acid (TPTC) comprises only isophthalic-acid-like terminations (meta-bonded −COOH groups), and forms into a random, entropically-driven lattice stabilized exclusively through bonds at the nonanoic acid/HOPG interface [108]. The random tiling exhibited by these molecules may arise from the symmetry of the molecule, which places the −COOH dimer bonds at the midpoint of rhombohedral tiles that can be mapped over each molecule within the lattice. The number of local structural geometries that can be supported through the strong hydrogen bonding gives rise to a complicated energy landscape of nearly-degenerate configurations, where defects can be observed to propagate through the network by STM in real time (i.e. on the order of seconds). A similar entropic-based crystallization was observed for a similarly-sized linear tetracarboxylic molecule (5,5'-(1,2-ethynediyl)bis(1,3-benzenedicarboxylic acid)) by Zhou et al, who found that slightly larger and slightly smaller molecules crystallized into a well-defined phase rather than a frustrated glassy network [109].

These examples from larger molecules show both the lessons and the limitations of studying a simple, small molecule like TMA. Although many of the motifs can be reproduced in other systems, the physical size of a molecule has important implications for the exposed surface area and lost molecule/surface adsorption enthalpy that can drive the system to bonding configurations where the strongest intermolecular bonding channel no longer dominates. Increasing the number of bonding sites from three to four can have implications for the regularity of the network, due to the increased number of degenerate bonding geometries.

4. Recent advances in hydrogen-bonded self-assembly of small carboxylated molecules: pattern formation from low-symmetry singly-carboxylated molecules

Molecules that possess only a single carboxylic group have not typically been the focus of self-assembly studies, since the formation of strong dimer bonds precludes the formation of spatially-extended hydrogen bonded layers. However, in recent years, investigations of singly-
Carboxylated molecules have revealed that they can offer insight into pattern formation and into the behaviour of their higher-functionalized counterparts.

In a 2014 publication by Wasio et al, Kandel’s group showed that the singly-carboxylated molecule ferrocenecarboxylic acid (FcCOOH) forms cyclic hydrogen bonds that echo the pentameric shape of the ferrocene scaffolding [110]. These five-fold hydrogen bonded assemblies densely pack on Au(1 1 1) following pulse deposition of FcCOOH from benzene solution under vacuum conditions. Analysis of STM images reveals that the FcCOOH films locally exhibit the 5- and 10-fold symmetry typical of quasicrystals, thus demonstrating the possibility for forming Penrose-like tilings using carboxylated building blocks.

The pulse-deposition technique used in this work creates a nonequilibrium deposition environment that can allow kinetically-favoured bonding configurations to dominate [111]. In follow-up work, the same group studied a dicarboxylated derivative of ferrocene, 1,1’-ferrocenedicarboxylic acid, Fc(COOH)₂, and determined that the hexamericlly-associated clusters that were found to dominate the molecular films likely originated in solution [112], a hypothesis which is supported by observation of the hexameric clusters in the molecular by electrospray-ionization mass spectrometry [113]. These clusters face kinetic barriers to reorganization on the surface, but annealing can transform a cluster-rich surface to one in which the molecules pack into extended ordered domains of more compact dimer-based structures [113].

The pentameric assemblies observed for FcCOOH also emerge as a motif for pulse-deposition of a non-fivefold symmetric molecule. In studies of indole-2-carboxylic acid (I2CA), Kandel’s group found that pulse-deposition onto Au(1 1 1) from solution in THF produced molecular pentamers, hexamers and extended linear assemblies that were identified as zig-zag hydrogen-bonded catemers [114]. In the case of the pentamers, DFT suggests that the cyclic hydrogen bonding is complemented by N–H...O bonds that further stabilize the structure. DFT of the catemeric chains indicates that while they are energetically uncompetitive with clusters for short (n < 6) chains, they become favourable for longer assemblies. The nonequilibrium deposition conditions clearly played a role in the formation of these structures; in an investigation of the same molecule following UHV deposition onto Au(1 1 1), we found that it produced extended domains of an ordered lamellar structure with a periodicity doubling due to chevron-like tilt variation of molecules in adjacent rows [115]. We interpreted this structure as comprising dimer bonds between the molecules in each lamella, and found the same basic structure in I2CA layers at the 1,2,4-tricholorobenzene/HOPG interface. Interestingly, at the heptanoic acid/HOPG interface I2CA forms an ordered structure with a completely different unit cell and appearance, which we hypothesized might arise from solvent coadsorption.

One key to increasing the complexity of patterns created by singly-carboxylated molecules is in their design. Low-symmetry molecules can dramatically increase the number of potential molecular configurations on the surface. For example, in our computational study of the
structure formed by the Cs-symmetric molecule I2CA on Au(1 1 1), we examined 16 different molecular configurations that could match the experimentally-observed unit cell [115], whereas a C2-symmetric molecule would have only offered a single corresponding geometry.

Secondary bonding channels can also augment the complexity of the energy landscape, and can easily be added, such as in molecules that include hydrogen bond donors or acceptors in addition to the −COOH. In the case of I2CA, the indole N–H serves this role. However, pyridinic-nitrogen-containing moieties introduce a new perturbation when positioned near to the −COOH group: the formation of zwitterions through transfer of the proton from the carboxylic group to the nitrogen. Kandel’s group investigated a trio of small, singly-carboxylated molecules including 2-naphthonic acid, and its pyridine-containing analogues quinaldic acid and 3-quinoline carboxylic acid [33]. Following pulse-deposition onto Au(1 1 1) from solution in methanol or toluene, the molecules exhibited markedly different behaviours. The 2-naphthonic acid formed dense layers comprising two primary motifs, pentamers and dimeric structures (figure 9(b)), whereas the quinaldic acid formed into clusters and assemblies based on dimers, tetramers and hexamers and 3-quinoline failed to produce layers with significant order. Analysis of the clusters formed by quinaldic acid suggests that they result from zwitterion formation. Zwitterions are usually stabilized by polar solvents, and their stability within molecular clusters on the surface suggests that perhaps intermolecular interactions or surface charge transfer can also play an important role in stabilizing the zwitterionic structure.

Figure 9. Pentameric motifs formed from (a) FcCOOH on Au(1 1 1) and (b) 2-naphthoic acid on Au(1 1 1) (highlighted in gold). Image sizes: (a) 205 × 205 Å (b) 350 × 350 Å. (a) Reprinted by permission Springer Nature Customer Service Centre GmbH: Nature [110] (2014). (b) Reproduced with permission from [33]. Copyright (2019) American Chemical Society.

5. Reactions of carboxylated molecules on surfaces

5.1. Deprotonation of carboxylic acids on surfaces

Small carboxylated molecules like TMA are frequently employed as the organic linkers in metal organic frameworks (MOFs) or other coordination structures because they can be easily deprotonated to their carboxylate form to act as a predictable linker of secondary bonding units [116]. In MOF synthesis, this typically occurs through solution-phase dissociation, but
deprotonation also occurs in surface-confined geometries, where it can lead to changes in bonding geometry and facilitate new self-assemblies.

5.1.1. Electrochemical studies.

Electrochemical studies can provide an illuminating glimpse into the both the hydrogen-bonded self-assembly and the deprotonation of carboxylated molecules at electrode surfaces; taking advantage of the electrified interface, assemblies can be selected and equilibrated for examination.

Studies of even the simplest carboxylated phenyl, benzoic acid, reveal a rich set of behaviours under electrochemical conditions. In 0.1 M HClO₄ acid solution on an Au(1 1 1) electrode, electrochemical STM shows that benzoic acid forms a number of potential-controlled self-assembled phases, with bonding stabilizing the planar-adsorbed assemblies formed at negatively-charged surfaces and positively-charged surfaces fostering a transition to upright adsorption of the benzoic acid via a gold-carboxylate interaction at short-bridge sites on the surface [117]. A similar potential-driven transition from symmetric dimers to upright adsorption was observed for benzoic acid in HClO₄ acid solution on Au(1 0 0) using electrochemical STM [118], and the potential control of both the flat-lying and upright adsorption geometries on gold electrodes has been substantiated by structure-sensitive techniques like infrared reflection absorption spectroscopy [119] and Raman spectroscopy [120].

Increasing the number of −COOH groups on the benzene core increases the complexity of the resulting pattern formation. For example, while TMA shows same overall trend of planar hydrogen-bonded assembly at negatively-polarized electrode surfaces and upright adsorption via carboxylate-metal interactions on positively-charged surfaces, a number of novel planar phases are found in electrochemical studies of TMA in 0.05 M H₂SO₄ on Au(1 1 1) [72]. These phases occur between the extreme of the chicken wire structure at high negative bias and the upright adsorption that occurs at positive bias. Each of these novel planar phases represents an energy minimization through higher-density packing in layers that comprise large unit cells and a range of TMA motifs including . The transition to upright adsorption of the deprotonated molecules at positive biases was confirmed by surface enhanced infrared reflection-absorption spectroscopy. The standing structure is stabilized by coordination to the surface via one carboxylate and the lateral stabilization of the structure through intermolecular hydrogen bonding [72]. Raman studies also show that the arrangement of TMA on electrode surfaces changes with bias voltage [121]. A study of TMA in 0.1 M HClO₄ confirmed that the observed TMA networks depend strongly on the applied potential, and clearly showed that different geometries arise from molecular and anionic adsorption, and that non-planar adsorption geometries occur due to carboxylate-surface interactions [122].

Although the same general themes arise from multiple electrochemical studies of carboxylated molecules, the parameter space for these experiments is very large, and a recent study demonstrates just how sensitive the obtained phases can be to molecular concentration,
electrochemical potential and electrolyte, in particular because of coadsorption of aqueous ions [123]. Together with the range of structures already observed, this interrelated dependency of parameters suggests that electrochemical deposition provides a unique toolkit to access assemblies not achievable through other conditions. However, the broad observations of these studies highlight an important implication of deprotonation of carboxylated molecules at metal surfaces: in electrochemical studies, the carboxylate group will often drive a transition in adsorption geometry by anchoring itself into the substrate, and as a consequence orienting other parts of the molecule away from the surface. Under electrochemical conditions, this orientation could be partially stabilized by the fields intrinsic in the electrochemical process, but as we will see later in this section, the same standing geometries can also be accomplished through both vacuum and solution processing, generally in cases where high packing density allows intermolecular interactions to stabilise the upright layers.

5.1.2. UHV studies.

The surface-catalysed deprotonation of carboxylic acids can result from the interaction of −COOH groups with a reactive substrate in vacuum. On a semiconductor surface, like Si(1 1 1)-(7 × 7), this occurs through hit-and-stick dissociative desorption, with strong interaction between the substrate and reacted molecule preventing diffusion and assembly into well-defined molecular architectures [124]. On metal surfaces, the role of the molecule-surface interactions has been demonstrated through XPS experiments showing that whereas first-layer molecules on Cu(1 1 1) and Pd(1 1 1) fully or partially deprotonate, molecules in a second layer remain intact [125]. The important role of the surface was also demonstrated through deposition of TPA onto clean Pd(1 1 1). Room temperature deposition reveals two coexisting phases: a 2D ribbon phase (denoted as α), which is attributed to fully deprotonated molecules stabilised through ionic hydrogen bonding, and a linear phase attributed to intact hydrogen-bonded molecules [125]. The coexistence of the two phases occurs due to the passivation of the Pd(1 1 1) surface through adsorption of hydrogen. Once the surface is hydrogen-terminated, either though hydrogen liberated by the deprotonation of TPA or by adsorption from vacuum, the surface is no longer sufficiently reactive to deprotonate the TPA and only the linear phase can form.

Adatoms, either intrinsic or extrinsic, can also promote deprotonation of −COOH. For example, flat-lying molecules are often observed to coordinate to adatoms following deprotonation [126]. The addition of extrinsic adatoms can induce reaction; for example, the reactivity of the relatively inert Au(1 1 1) surface was increased through the introduction of additional Cu adatoms, which facilitated the deprotonation of −COOH from TMA [127]. The coordination of deprotonated molecules to metal adatoms constitutes the basis of carboxylate-based surface-confined coordination networks, which have recently been reviewed in detail [12], and so will not be covered in depth here. However, it is important to note that these adatom-coordinated structures may provide a design strategy for enzyme-like materials to address emerging
challenges in heterocatalysis [128]. Hence, there is considerable interest in developing approaches for coordinating different metal atoms, and carboxylate groups appear to be good candidates as ligands. For example, on Cu(0 0 1) TPA forms well-defined coordination networks with Fe [129], and recent work showed that the f-block element gadolinium can be coordinated into a 2D structure by 4,1′,4′,1′′-terphenyl-1,4′′-dicarboxylic acid on Cu(1 1 1), demonstrating the feasibility of lanthanide-carboxylate interactions for architectures on metallic surfaces [130].

Coordination to surface atoms, rather than adatoms, can also allow the formation of phases with flat-lying molecules. Following deposition onto Cu(0 0 1) at 190 K, submonolayer coverages of TPA successively deprotonate with annealing to 400 K, at which point the molecule is fully deprotonated [131]. STM shows three distinct, flat-lying molecular self-assemblies at increasing temperature, which were originally thought to correspond to intact, intermediate, and fully-deprotonated molecules [131]. Recent work suggests that deprotonation is ubiquitous for this system, with even the α-phase formed at 190 K comprising deprotonated molecules [132]. The fully-deprotonated TPA islands are compact and tightly-packed, and coexist with bare Cu regions [133]. A study combining experiment and DFT determined that the strong interaction between the carboxylate and the underlying copper substrate produces a buckling of the fully-deprotonated TPA molecules, which take on an arched shape due to the close O-Cu contacts [134].

Studies of other small carboxylated molecules on different copper facets reveal modifications to both chemistry and adsorption geometry with annealing, emphasizing that while the formation of carboxylate from carboxylic may drive changes to molecular superstructure by modifying the molecule-substrate interaction channel, molecule–molecule interaction can provide a secondary stabilization that depends on coverage. For example, on Cu(1 1 0), the motif defined by the deprotonated TMA depends on both the coverage and the annealing temperature, with higher coverages leading to a standing phase [126]. TPA behaves similarly on Cu(1 1 0), with flat adsorption at low coverage and a standing phase, anchored via carboxylate/substrate interactions, at higher coverage [135]. DFT calculations show that it is not energetically favourable for the molecules in the standing phase to hydrogen bond to one another [135]. Hence, this standing geometry puts TPA in a favourable position for the subsequent reaction of the upward-facing −COOH, which creates opportunities for novel nano-engineering starting from a layer of upright carboxylated molecules.

Another interesting possibility for application arises based on the orientation of the −OH bond in the upward-facing −COOH group. Calculations suggest that when 2,5-pyridine dicarboxylic acid is anchored to Cu(1 1 0) via a carboxylate, changing the orientation of the −OH group in the upward-facing −COOH group from pointing towards the aromatic ring to pointing out of the surface can modify the work function by 2.5 eV [136]. Hence, carboxylated molecules might be useful contenders for organic layers that can be used to tune surface electronic properties since these upright phases with free carboxylic groups protruding from the upper interface
have been observed a number of times. For example, 2,5-pyridine dicarboxylic acid forms an upright carboxylate-anchored phase on TiO$_2$(1 1 0)–(1 × 1) [137], we observed a similar phase for 3,5-pyridine dicarboxylic acid on Cu(1 1 1) [138].

5.1.3. Reactions in the solution-phase.

Since solution processing occurs outside of vacuum, the substrates of choice tend to be non-reactive and therefore to limit the possibility for observing reactions in carboxylated molecules. However, a solution-based approach can be used to induce deprotonation even on a non-reactive substrate in solution through the addition of metal ions. For example, Li et al hypothesize that deprotonation of TMA and the subsequent formation of coordination-based architectures occurs at the nonanoic acid/HOPG interface through the addition of nitrate salts to the solution [139]. They show that the TMA chicken wire mesh is unperturbed by the presence of filled-orbital salts (Ag(NO$_3$)$_2$, Zn(NO$_3$)$_2$), which remain intact and occupy the guest sites in the pores [139]. Salts with non-filled orbitals (Cu(NO$_3$)$_2$, Mn(NO$_3$)$_2$, Fe(NO$_3$)$_3$) seem to dissociate to produce new geometries that the authors hypothesize are stabilized by coordination of the metal ions [139].

Another successful approach to facilitating molecular reactions in solution processing relies on using electrochemistry to deposit thin layers of Cu or Ag onto Au(1 1 1) films through underpotential deposition (UPD) [140]. This process results in substrates that are more reactive than Au(1 1 1) but not as prone to oxidation as Cu or Au bulk-terminated samples, meaning that they are amenable to ambient handling and solution-phase deposition of molecules [141]. Buck et al have used these UPD layers to study the solution-phase deposition, reaction and assembly of a range of carboxylated molecules. For example, both TMA and IPA self-assemble into a row-like 3 × √3 structure on a Au(1 1 1) surface modified by UPD of Cu to produce ~0.66 ML coverage of the metal layer. By investigating with STM and XPS, the authors suggest that the structure involves the upright adsorption of the molecule through carboxylate binding to the surface, based on the appearance in STM images and the XPS signature of complete (IPA) or partial (TMA) deprotonation of the −COOH groups [39]. In later works the group used NEXAFS to confirm the adsorption geometry of the same two molecules on Au(1 1 1) modified by UPD Cu and Ag, and found some interesting differences [38]. Both IPA and TMA adsorb via two carboxylate groups on the Cu-modified the surface, whereas they exhibit lower deprotonation on Ag-modified surfaces, leading the authors to suggest that they bind to the surface through a single carboxylate only. In addition, NEXAFS indicates that the adsorption geometries are quite different between the two surfaces, with the Ag-modified surface presenting more upright molecules than the Cu-modified surface. The authors ascribe these differences primarily to the lower strength of the carboxylate-metal coordination bond on Ag.

As in the case of the hydrogen-bonded structures formed from TMA (see section 3.1.3), the lessons learned from this simple molecule can be better contextualized by considering molecules that represent slight perturbations from TMA's compact, highly-symmetric structure. Buck et al have studied two of the same molecules previously examined in the context of
hydrogen bonding: H3BHTC and BTB. In the case of H3BHTC, the behaviour of TMA is a strong predictor for the behaviour of the larger, lower-symmetry molecule. H3BHTC bonds to UPD Cu-modified Au(1 1 1) via two carboxylate coordination bonds, but it bonds to Ag-modified Au(1 1 1) through only a single bond [37]. The molecule predictably adsorbs on its meta-bonded −COOH groups on the Cu-terminated surface, but exhibits polymorphism on the Ag-terminated surface, where different configurations are possible for adsorption via a single carboxylate, and where interactions between intact −COOH groups appear to add additional stabilization. For BTB, this intermolecular hydrogen bonding becomes even more important: BTB forms an ordered 3 × √3 row structure on Ag-modified Au(1 1 1), anchored by a single carboxylate-metal bond to the substrate and with inter-row interactions through the elevated −COOH groups further stabilising the structure (figure 10) [35]. Interestingly, BTB fails to form an ordered layer on the Cu-modified surface. A follow up work in which mono- and dicarboxylated para-oligophenylenes were studied on UPD Ag on Au(1 1 1) suggests that intermolecular interactions are critical for determining the structure on this surfaces [36]. Like the other systems studied on Ag on Au(1 1 1), the molecules anchor through a single substrate-carboxylate bond. However, whereas the monocarboxylic acids exhibit a (5 × √3) structure, the dicarboxylic acids describe an oblique (√93 × √133) unit cell, and DFT calculations suggest that intermolecular hydrogen bonding arising from the intact −COOH groups drives the difference.

![Figure 10. BTB on UPD Ag on Au(1 1 1). (a), (b) STM images of the linear structure, showing the degenerate domains and the orientation with respect to substrate lattice directions. (c) A model based on NEXAFS and XPS, where the molecule is bound to the surface through a carboxylate. Reproduced from [35] with permission of The Royal Society of Chemistry.](image)

The upright adsorption of molecules that retain free −COOH groups is a basic design strategy for designing surface-bound 3D organic assemblies, an application that is discussed further in section 6.2.

### 5.2. Complex assemblies from partially deprotonated molecules
Multiple interaction pathways within a single molecule can lead to a wide array of possible stable architectures on a surface [142]. In our recent work, we found that the multiple interaction pathways intrinsic to a partially-deprotonated TMA molecule can lead to fascinating and complex assemblies on Ag(1 1 1). Following deposition onto Ag(1 1 1), we heated the TMA and observed both the chemistry (via XPS) and the structure (via UHV STM) of the resulting overlayer. Between average deprotonation levels of ~25% and ~90%, we observed the formation of a chiral, non-periodic self-assembly that had as its basic building block a bright protrusion around which six triangular features were coordinated, which we termed a pinwheel; a single pinwheel is outlined in white in figure 11(a) [143]. At low levels of deprotonation, these features were separated from one another, but as deprotonation increased the features began to knit together. By inspection of high-resolution STM images together with chemical information from XPS, we attributed the six-molecule building block to the coordination of −COO− to a central Ag atom or atoms. In the discrete pinwheel phase, the intact −COOH groups of each TMA molecule are at the exterior of the pinwheel, and interact with other pinwheels on the surface through hydrogen bonding. With increased annealing, more and more of the −COOH groups deprotonate, and discrete pinwheels grow together into a compact, fully-knitted pinwheel phase (figure 11(c)). The discrete and knitted pinwheel phases have unit cells that allow for the seamless integration of the two phases, even without long-range order, and assert a chirality that relates to the rotation of the TMA scaffolds with respect to the overlayer unit cell, and which propagates across domains. Between the discrete and knitted pinwheel phases exists a fascinating phase that demonstrates the possibility for controlled formation of non-periodic structures (figures 11(b) and (d)). This phase also demonstrates an interesting nano-cluster coordination motif: follow-up work showed that the bright protrusions at the centre of the pinwheels are due to seven-atom silver clusters, with different partial charges on the inner and outer atoms [50].
Figure 11. Nonperiodic and periodic phases formed by the successive deprotonation of TMA on Ag(1 1 1). (a) A predominantly discrete pinwheel phase, which arises when deprotonation is close to 33%. (b) A composite phase, where many pinwheels have begun to coalesce into the knitted pinwheel phase. (c) The knitted pinwheel phase, which corresponds to 100% deprotonation. (d) The long-range lack of order in the composite phases, with the inset FFT demonstrating how the unit cells of the phases are rotated with respect to one another. STM parameters: All images 8 x 8 nm$^2$ in size, (a) $I_T = 50$ pA, $V_B = -50$ mV, (b) $I_T = 50$ pA, $V_B = -50$ mV, (c) $I_T = 250$ pA, $V_B = -250$ mV. Reproduced from [143]. CC BY 3.0.

Cao et al demonstrated that deprotonation can be used to drive complex layer structures on Ag(1 1 1) using the larger molecule 1,3,5-tris(4-carboxyphenyl)benzene (TCPB) in coassembly with 4,4”-diaminop-terphenyl (DATP) [144]. In this case, the successive deprotonation of TCPB led to denser and denser packing of TCPB/DATP cocrystals. This mirrors the denser and denser packing that the authors show for TCPB alone, which transitions from a chicken wire phase formed from fully-intact molecules, to a ribbon-like phase of partially-deprotonated molecules, to a close-packed phase of fully-deprotonated molecules. Integration of the DATP into the molecular layer shows that the deprotonation of carboxylated molecules can be used to drive the properties in bi-component systems, and hints that this may be a way to control layer interactions and geometries.

5.3. C–C bond formation on surfaces
Graphene and related 2D materials have already begun to revolutionize nanoscale devices, from batteries and other forms of energy storage to sensors and electronics, and stand to enable a new generation of novel technologies [145]. Single-atom thick materials represent the physical limit of miniaturization (no thinner material is conceivable), and can possess remarkable functional properties: graphene is both stronger than almost any other material, and has unprecedented electron transport properties [146]. However, graphene is a gapless semimetal rather than a semiconductor, and hence other 2D materials like chalcogenides [147] are being actively explored for applications where an electronic gap is required. These and other classes of 2D materials have a fundamental similarity: they are structurally and stoichiometrically well-defined inorganic materials with relatively small and simple unit cells. Post-processing is necessary to functionalize these materials or to introduce pores or other structural modifications, and precise control over the outcome of these processes remains challenging. Another approach to creating energy gaps in 2D materials relies on techniques of synthetic chemistry: organic polymers are emerging as a new class of 2D materials that can be designed with bespoke properties, including functionalization, without need for post-processing. The synthesis of engineered 2D polymeric materials with specific physical and chemical properties can be achieved by starting from purpose-built organic building blocks.

One particularly successful synthesis approach for these materials is to use reversible condensation reactions to produce covalent organic frameworks (COFs); by manipulating the chemical equilibrium, self-healing can be exploited to produce COFs with exceptional crystalline quality and with a wide range of structural and chemical characteristics [148]. These condensation reactions tend to proceed without the need for catalysts, and COF synthesis can be translated quite simply to a surface-confined geometry that facilitates the growth of single-layer polymers. However, these materials are not amenable to all applications: they have large electronic gaps (~7.94 eV for COF-1, a prototypical COF) [149], and COFs formed through water-evolving condensation reactions are unstable with respect to humidity and aqueous environments.

To grow 2D polymers with good electronic characteristics (i.e. semiconducting polymers with delocalization of electrons through extended $\pi$-conjugation), on-surface synthesis via irreversible C–C or C–N coupling reactions can be facilitated by using a metal surface to both support and template the reactants/products in 2D and to catalyse the reaction [150]. This approach can, e.g. lead to the formation of high-quality graphene nanoribbons from carefully-designed precursors [151]. To date, much of the work in on-surface synthesis has focused on Ullmann coupling and Schiff-base reactions, but in recent years decarboxylative coupling has also emerged as a viable approach to on-surface synthesis of polymers. We review this progress below.

5.3.1. 1D structures through decarboxylation.
The possibility of using decarboxylation as a route to on-surface covalent coupling was first investigated by Gao et al., who showed that 2,6-naphthalenedicarboxylic acid can covalently couple on metal surfaces following successive reaction of the monomer [152]. The monomer first deprotonates to form a carboxylate-metal coordination bond between planar-adsorbed molecules, then decarboxylates to form an organometallic, and finally forms a covalently coupled polymer following ejection of the metal centres [152]. The authors investigated this process on multiple surfaces, and found the reactivity of the surfaces to decrease from Cu(1 1 1) to Cu(1 0 0) to Ag(1 1 1) to Cu(1 1 0) to Au(1 1 1), with both redox ability and adatom availability playing roles in this ordering.

In the work from Gao et al, the substrate symmetry was shown to have a defining effect on the disposition of the polymer product on the surfaces. In a 2018 work, Wu et al. used the surface symmetry to their advantage, and demonstrated the formation of extended, aligned aliphatic hydrocarbons following decarboxylative coupling of C\textsubscript{30}H\textsubscript{60}O\textsubscript{2} on Au(1 1 0) [153]. Using XPS and STM, they showed that the reaction follows the same deprotonation-decarboxylation pathway as was reported by Gao et al., and that the resulting polymers extend along the surface furrows. A decarboxylative approach was also used to form armchair graphene ribbons five atoms wide through the coupling of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on Cu(1 1 1) [154]. After room-temperature deposition, the PTCDA exhibited its known self-assembled phase, whereas depositing onto a surface held at ~250 °C produced linear structures. The contrast and spacing observed in STM images led the investigators to interpret these as organometallic structures, with two copper atoms bridging the decarboxylated PTCDA molecules. Further annealing to ~350 °C produces structures with the appearance and width of five-atom armchair graphene nanoribbons. Although it results in only a yield of about 20%, this appears to be a promising pathway for nanoribbon formation. PTCDA-based molecules have also been investigated in other contexts for nanoribbon formation: the halogenated molecule 1,6,7,12-tetrabromo-3,4,9,10-perylene-tetracarboxylic-dianhydride (Br\textsubscript{4}-PTCDA) was investigated on Au(1 1 1), and shown to form graphene-like ribbons with embedded four- and eight-fold rings following annealing to 360 °C [155]. In this case, however, the coupling was due to debromination and cyclodehydrogenation, and the reaction process left the carboxylic anhydride groups intact, emphasizing the temperature and surface-dependence of on-surface reactions.

5.3.2. 2D structures through decarboxylation.

Decarboxylative coupling can be applied to molecules with three reactive sites to extend polymer formation into two dimensions. Morchutt et al. showed that BTB adsorbed at RT on Cu(1 1 1) arranges into a closely-packed, fully-deprotonated layer, and that subsequent annealing at 180 °C induces decarboxylation and subsequent coupling of the reactive species into 2D polymers [156]. The polymer networks are disordered, comprising both the expected large hexagonal pores attributable to decarboxylation and smaller pores consisted with covalent bonding following dehydrogenation at hydrogens adjacent to the carboxylic
terminations. This sort of dehydrogenation had been observed previously, for example, where proximity to the $-\text{OH}$ of a phenol group was used to selectively drive dehydrogenation in the ortho position of different molecules [157]. Furthermore, we observed the same effect in the disordered covalent polymers formed by the decarboxylative coupling of TMA on Cu(1 1 1) [158]. These early results suggest that achieving ordered structures from decarboxylative coupling may, at least on Cu(1 1 1), be a challenge due to the non-uniqueness of the covalent bonding site.

6. Emerging applications of nanoarchitectures based on assembly and reactions of carboxylated molecules on surfaces

Understanding the behaviour of carboxylated molecules at surfaces is foundational to establishing control of their 2D patterns, and may also help lay the groundwork for understanding related molecules with targeted applications. For example, the $-\text{OH}/=\text{O}$ functionalized molecule croconic acid is ferroelectric as a hydrogen-bonded 3D crystal [159], and recent investigations have revealed the formation of surface-supported 2D croconic acid networks [160] and cocrystals [161] that are in many ways analogous to carboxylated networks. However, in addition to this type of potentially-transferrable fundamental knowledge based on investigations of carboxylated molecules, a number of studies have begun directly exploring their use in the context of applications.

6.1. Molecular self-assembly for noncovalent modification of 2D materials.

Noncovalent modification is an attractive pathway to tailoring the properties of 2D materials since covalent modification can disrupt the structure and properties of the 2D material in detrimental ways, e.g. by interrupting the conjugation in graphene [162]. Conversely, non-covalent modification can often be performed under mild conditions, and leaves the structure of the original 2D material intact; molecular self-assembly at the surface of the 2D material is emerging as an interesting possibility for achieving this result [163]. Recent work even shows that self-assembled molecular networks can be applied in alternating layers with 2D materials, allowing the formation of bespoke heterostructures comprising both molecular layers and 2D materials [164].

To date, studies of the noncovalent functionalization of 2D materials have tended to focus on molecules with pronounced electronic effects, such as the electron-withdrawing molecule tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F$_4$-TCNQ) or metalloporphyrins [165]. However, small carboxylated molecules like TMA may offer a unique advantage in modifying the electronic properties of 2D materials, since their polymorphism can be used to adjust the symmetry and packing of the molecule on the surface. A theoretical study by Shayeganfar and Rochefort suggested that adsorption of TMA on graphene would result in p-type doping and bandgap opening, with the doping depending on the areal density of TMA and the bandgap opening depending on the specific pattern that the TMA defines within its overlayer structure.
When adsorbed on bilayer graphene, an individual TMA is predicted to accept 0.2e from the underlying graphene, with a charge difference between the top and bottom layers of the graphene bilayer producing a built-in electric field [167]. The same work finds that self-assembled layers of TMA on bilayer graphene should allow tuning of the bandgap.

These studies hint at a key role for carboxylic-based assemblies to play in electronic modification of materials. Since the geometries of assemblies can be controlled through processing conditions, even a simple molecule (like TMA) can be used alone to provide tuned modification to the electronic structure. The possibilities expand when we consider host-guest structures where the host lattice and guest molecules are chosen to provide either a uniform or periodic modulation of the electronic structure.

### 6.2. 2D layers as foundations for out-of-plane structures

Recently, Johnson et al. investigated the assembly of three different non-planar tetracarboxylated molecules on HOPG and Au(1 1 1): tetraphenylethene tetracarboxylic acid (ETC), tetraphenylethene tetrakis-phenyl carboxylic acid (ETTC), and tetraphenylethene bisphenyl carboxylic acid (BPDC) [168]. On Au(1 1 1), they observed the formation of condensed lamellar structures, which they attributed to the adsorption of the molecules via $-\text{COO}^-$ metal coordination at the substrate, showing that it is possible to achieve an upright adsorption geometry with free $-\text{COOH}$ groups through a simple solution-based process using an as-received Au(1 1 1) substrate. Their hypothesized structure for the ETTC layer is shown in figure 12; the phase is stabilized through a combination of interactions, including surface adsorption and formation of an interface dipole that leads to dipole-dipole repulsions between neighbouring lamellae.

![Figure 12](image-url)  
**Figure 12.** Upright adsorption of the tetracarboxylic acid ETTC at the heptanoic acid/Au(1 1 1) interface. Johnson et al. hypothesize that dipoles form between the carboxylate groups and the substrate, and that these dictate lamellar spacing through dipole-dipole interactions. Reprinted with permission from [168]. Copyright (2019) American Chemical Society.

The use of carboxylic-based layers as a foundation for the growth of out-of-plane structures has been explored by Buck’s group, who demonstrated the early stages of MOF growth on top of a TMA layer adsorbed on UPD Cu on Au(1 1 1) [38]. By successively exposing the TMA layer to Cu-acetate and additional TMA, they were able to observe new features in STM images that
they attributed to the formation of metal-organic bridges based on second-layer growth of TMA via carboxylate bridges. Their proposed structure is conceptually similar to the HKUST-1 MOF, which is based on a dicopper(II) tetracarboxylate building block comprising four TMA molecules [169].

6.3. Tribological applications
Molecular layers are appealing candidates as coatings to reduce friction [170], and 2D self-assembled layers have the advantage of potentially being atomically thin and self-healing, due to the reversibility of their non-covalent bonding. Recently, Shi et al carried out an AFM-based investigation of the nanotribological properties of self-assembled molecular layers on graphene, where they looked at the friction force associated with both TMA and BTB layers on HOPG [171]. In their study, the solution-processed layers produced TMA in a chicken wire bonding configuration, and BTB in a dimer phase with weaker −COOH bonding (see figure 13). The nanoscale measurements of friction revealed higher friction in the TMA network than the BTB network, a phenomenon that the authors attribute to the higher energetic stability of the TMA network. They note that both molecule-substrate and molecule–molecule interactions contribute to this effect, and suggest the frictional energy dissipation process relies on the continual breaking and regeneration of bonds within the layer.

Figure 13. Molecular structures for (a) TMA and (b) BTB, and (c) the resulting friction as a function of load for each of these layers on HOPG as measured by AFM. Reprinted with permission from [171]. Copyright (2018) American Chemical Society.

7. Conclusions and outlook
Small, carboxylated molecules present an ideal testing ground for exploring and establishing design strategies in 2D molecular materials, where the energetics of molecule–molecule interactions work in tandem with contributions from molecular adsorption on the substrate. Hydrogen bonding interactions enable the ability for complex pattern-making in 2D. The $-\text{COOH}$ groups provide a strong, predictable $R_\text{S}^2(8)$ bonding channel, but this can be subverted by employing molecules that can offer higher-density packing through lower-enthalpy bonding configurations. C3-symmetric, carboxylic-terminated molecules can be used to define porous templates that are amenable to hosting guest molecules, allowing the creation of bimolecular arrays. Bimolecular architectures can also be implemented by mixing two hydrogen-bonding units on the surface, where they can create ordered or disordered cocrystals. Control of processing conditions can enable the formation of different types of bonding and ring-bonded structures.

The $-\text{COOH}$ group can successively react to form carboxylate ($-\text{COO}^-$) and then to dissociate from the molecule entirely, providing access to the stronger interactions associated with metal-organic coordination and covalent bond formation, respectively. Deprotonation can be facilitated through various processing routes, including in solution or through interaction with a reactive surface. Molecular reorientation upon deprotonation allows interaction of the carboxylate group with substrate metal atoms or adatoms, and leaves non-carboxylate functional groups available for interaction and for building new architectures out of plane. In planar adsorption geometries, coordination architectures can reveal a wealth of patterns and can potentially create arrays of adatoms with useful applications. Decarboxylation is now being explored as a 'clean' approach to forming surface polymers, and may take up a useful place in the toolbox of synthesis approaches.

Small, carboxylic-functionalized molecules thus provide a window into the opportunities for materials design and synthesis using organic building blocks constrained to a 2D plane. As the need for new materials continues to grow, so will our need to advance our knowledge and application of on-surface assemblies and reactions, which means that further study of these systems remains a priority.

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