Topical Review

Molecular assembly on two-dimensional materials

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Abstract

Molecular self-assembly is a well-known technique to create highly functional nanostructures on surfaces. Self-assembly on two-dimensional (2D) materials is a developing field driven by the interest in functionalization of 2D materials in order to tune their electronic properties. This has resulted in the discovery of several rich and interesting phenomena. Here, we review this progress with an emphasis on the electronic properties of the adsorbates and the substrate in well-defined systems, as unveiled by scanning tunneling microscopy. The review covers three aspects of the self-assembly. The first one focuses on non-covalent self-assembly dealing with site-selectivity due to inherent moiré pattern present on 2D materials grown on substrates. We also see that modification of intermolecular interactions and molecule–substrate interactions influences the assembly drastically and that 2D materials can also be used as a platform to carry out covalent and metal-coordinated assembly. The second part deals with the electronic properties of molecules adsorbed on 2D materials. By virtue of being inert and possessing low density of states near the Fermi level, 2D materials decouple molecules electronically from the underlying metal substrate and allow high-resolution spectroscopy and imaging of molecular orbitals. The moiré pattern on the 2D materials causes site-selective gating and charging of molecules in some cases. The last section covers the effects of self-assembled, acceptor and donor type, organic molecules on the electronic properties of graphene as revealed by spectroscopy and electrical transport measurements. Non-covalent functionalization of 2D materials has already been applied for their application as catalysts and sensors. With the current surge of activity on building van der Waals heterostructures from atomically thin crystals, molecular self-assembly has the potential to add an extra level of flexibility and functionality for applications ranging from flexible electronics and OLEDs to novel electronic devices and spintronics.

Keywords: molecular self-assembly, two-dimensional materials, graphene, hexagonal boron nitride, scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS)

(Some figures may appear in colour only in the online journal)

1. Introduction

Molecular self-assembly on solid surfaces have been studied with an aim to create ultra-high density functional nanostructures which can be fabricated in a parallel fashion. Structure of such assembly is driven by the interplay of the intermolecular and molecule–substrate interactions. On weakly interacting surfaces, molecules typically interact with substrate only through van der Waals (vdW) interactions; the structure of the assembly is then determined by intermolecular forces. For example, vdW forces result in close-packed assemblies where the symmetry is determined by the geometry of adsorbed molecules [1], while slightly stronger and directional interactions (e.g. hydrogen, metal-coordination, or...
covalent bonds) lead to structures with more varied and open assembling motifs [2, 3]. This simple picture changes on interacting substrates, where the surface is not an innocent bystander [4]. In extreme cases, native metal adatoms can be incorporated into the network [5] or adsorbate induced reconstruction of the surface can lead to new self-assembly 

insulating substrates e.g., silicon dioxide, graphene is most relevant on technologically important, sensors. This implies that the study of molecular assembly on properties, boosting its potential applications in electronics or adlayers has been suggested as means of tailoring graphene.

Molecular self-assemblies can be fundamentally different in the case of two-dimensional (2D) materials, such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDCs), which have attracted enormous interest recently [8–10]. The study of atomically thin crystals has been initially dominated by research on graphene. Graphene consists of sp² hybridized carbon atoms in a triangular lattice with a two-atom unit cell. The out-of-plane π orbitals form delocalized bonding π and antibonding π* bands. These bands touch at the K- and K’-points of the Brillouin zone (also known as the Dirac points) resulting in a linear dispersion of the charge carriers that renders graphene a zero band gap semimetal [11]. The rise of graphene has been closely followed by that of monolayer hBN. It is isostрукular to graphene, with boron and nitrogen, instead of carbon, forming the basis of a similar triangular lattice (the lattice parameters of graphene and hBN differ by 1.8%) [12]. Unlike graphene, hBN is an insulator with a band gap of ~6 eV. Monolayers of TMDCs are the latest entrant to the family of 2D crystals and a lot of work is going on to unravel the unique properties of these atomically thin materials [13]. Although the spectrum of 2D material is expanding rapidly [14], the study of molecular self-assembly has so far, to a large degree, been concentrated on graphene and hBN only.

Investigation of adsorbed single molecules and assemblies on 2D materials is important for several reasons. Essentially all of the atoms on these materials are on the surface; hence, covalent or even non-covalent functionalization can completely change their physical and electronic properties [15]. This has already been shown for graphene where covalent functionalization using hydrogen, oxygen, or fluorine has modified the electronic properties with the functionalized carbon atoms being rehybridized from sp² to sp³ [16–18]. Non-covalent functionalization using molecular adlayers has been suggested as means of tailoring graphene’s band structure without compromising its excellent electronic properties, boosting its potential applications in electronics or sensors. This implies that the study of molecular assembly on graphene is most relevant on technologically important, insulating substrates e.g., silicon dioxide (SiO₂) or bulk hBN for real device applications. Also at very nascent stage of research, chemical functionalization of TMDCs have shown to alter their electronic properties [19]. In general, chemical functionalization can be used to engineer 2D materials in devices through formation of surface dipoles, charge transfer, energy band alignment, and orbital interactions. Molecular adlayers can help enable novel applications that are only made possible through the unique properties of 2D materials.

Secondly, both graphene and hBN offer inert surfaces on which the fundamental principles of surface assembly can be verified. Close-packed molecular assemblies with weak intermolecular bonds or hydrogen-bonded networks have been studied extensively on graphene—reviews of such studies can be found in [20, 21]. An important point here is that the bulk substrate supporting the atomically thin 2D material can have a significant effect on the molecular assembly. As we discuss in section 2, the structural and electronic landscape of both epitaxial graphene and hBN is intimately dependent on the surface on which it is grown. Periodic structural, as well as electronic corrugation, on these surfaces can lead to highly site-selective molecular adsorption—examples will be given in section 3.1. Section 3.2 describes close-packed assembly on epitaxial graphene while section 3.3 offers engineering aspects of assembly on 2D materials. The first layer of molecular network has often been used to form templates for multi-component, hierarchical growth of molecules—these phenomena will be discussed in section 3.4. Studies on chemical reactions of molecules on graphene and hBN will be reviewed in section 3.5.

Furthermore, due to their inertness, graphene and hBN can be used as ultrathin decoupling layers. Low-temperature scanning tunneling microscopy (STM) studies make it possible to resolve intramolecular features; increased lifetime of injected electrons results in narrow spectral features and make it possible to visualize molecular orbitals in real space. In section 4, the rich field of using graphene and hBN as substrates in the study of single-molecules will be explored. Section 4.1 illustrates orbital imaging of molecules on 2D materials. On strongly site-selective assemblies, the electronic properties of the molecules are modulated according to the potential landscape of the underlying 2D material as will be shown in section 4.2. In some cases, the electric field from the STM tip can lead to charging of the molecule (gating) on the surface, this effect has been illustrated in section 4.3.

After the discussion on molecular self-assembly on epitaxial layers of 2D materials, we turn to the technologically more relevant systems where the 2D material has been deposited on insulating substrates. Some examples of direct, scanning-probe observation of molecular self-assembly on such substrates will be summarized in section 3.2. The effect of molecular layers on the electronic properties of graphene on such samples has been studied using photoelectron spectroscopy (PES), Raman spectroscopy, and current–voltage (I – V) measurements on graphene field-effect transistors (FETs). These results will be summarized in section 5.

This review is limited to the studies of ordered adlayers of molecules on 2D materials, primarily graphene and hBN. The emphasis is on the electronic effects of the assembled molecules (and the surface underneath) principally investigated by STM in ultra-high vacuum conditions at low temperature. For a more general review of molecular assembly on graphene readers are directed to [20, 21]. Non-covalent functionalization of graphene is a vast field and has been reviewed extensively in [22–26]. Review of covalent approaches toward functionalizing graphene can be found in [16, 21, 27–29]. Finally, surface functionalization of TMDCs...
and 2D materials other than graphene has been reviewed in [19, 30–32].

2. 2D materials

2D crystals are only one atomic layer thick and hence, for most practical purposes they have to be supported by a bulk substrate. The nature of the support and its interaction with the 2D material are important in determining the surface electronic structure and, through the molecule–substrate interactions, it also affects molecular self-assembly. Graphene, the first 2D material to be discovered, was first obtained by means of mechanical exfoliation of graphite onto SiO2 surface. Since then, other means of producing graphene (e.g., chemical exfoliation of graphite, chemical vapor deposition (CVD) on metals) and transferring it onto insulating substrates (e.g., SiO2, bulk hBN, polymers) have emerged [33]. In recent years, graphene (produced by exfoliation or CVD) transferred onto bulk hBN has attracted a lot of attention as many properties of free-standing graphene are retained on hBN and it has emerged as the de facto standard substrate in the highest performance graphene devices [34, 35]. The atomically smooth surface of graphene on hBN presents the ideal surface on which molecular self-assembly on graphene can be tested. However, the transfer processes involved can result in contamination of the graphene surface, which naturally hinders precise studies of molecular self-assembly.

Graphene for studies on molecular self-assembly in well-defined and controlled environment (ultra-high vacuum, UHV) is mostly obtained in situ via epitaxial growth on single crystals. Graphene can be grown by thermal sublimation of silicon from silicon carbide (6H-SiC(0001)) crystals [36] or by thermal decomposition of hydrocarbons on the hexagonal surfaces (FCC(111) or HCP(0001)) of transition metal single crystals [37]. Recently, some methods for the direct growth of graphene on insulating substrates have also been presented [38]. The substrate can have a significant effect on properties of the epitaxial graphene layer and the substrates can be classified into weakly and strongly interacting ones. Single layer graphene grown on SiC (G/SiC) is weakly coupled to the substrate due to an interfacial carbon buffer layer, which is covalently bonded with underlying silicon atoms [39–41]. The graphene-substrate distance (3.3 Å) [42] is close to the inter-layer separation in graphite. This indicates that the graphene interacts with the substrate only through vdW forces, which is reflected in the electronic properties being close to those of free-standing graphene [43]. On the other hand, the interaction of graphene grown on metals depends on the substrate and has been discussed in detail in [37, 44]. Graphene-metal systems with a lattice mismatch gives rise to a long-range, periodic superstructure called the moiré pattern. The geometry and electronic properties of graphene vary over the moiré unit cell due to the periodically modulated carbon adsorption site w.r.t. the metal substrate. In the regions where the center of the carbon ring sits on top of the surface metal atom, the carbon-metal interaction is typically weak—near these regions (so-called TOP-site) the graphene sheet is the farthest away from the metal surface. On the other hand, when alternate carbon atoms are positioned over the surface metal atoms, strong interaction between them leads to a lower adsorption height of the graphene sheet (valley site). In the low lying areas of the moiré further differentiation can be made on the basis of whether the carbon atoms not on top of metal atoms are on the FCC-hollow site (FCC-site), the HCP-hollow site (HCP-site), or in between these sites (bridge site) of the surface metal atoms. This is shown in figure 1(a).

Within the limit of this periodic variation, if the mean graphene-metal distance (Δavg) is large, as in the case of
graphene on iridium (G/Ir(111) \sim 3.4 \text{ Å}) or platinum (G/Pt (111) \sim 3.3 \text{ Å}), the resulting system is a weakly interacting \cite{45–48}. In these systems the topographic corrugation (\Delta_{corr}) over the moiré unit cell is small (<0.5 \text{ Å}) and graphene retains its linear dispersion. Conversely, graphene grown on ruthenium (G/Ru(0001)) or rhodium (G/Rh(111)) interact strongly with the metal, and the graphene-metal distance varies from \sim 2.1 \text{ Å} in the bridge sites (significant carbon-metal hybridization) to >3.6 \text{ Å} at the TOP sites (free-standing graphene) \cite{49, 50}. This is accompanied by a variation of work function of 0.32 eV across the moiré unit cell and has profound implications in terms of adsorption energy of molecules at the different moiré sites. The lattice matched graphene-nickel (G/Ni(111)) system which does not show any superstructure because of 1 \times 1 commensurate growth is another example of strongly interacting graphene \cite{51–53}. The electronic properties of graphene on strongly interacting metals are strongly modified, including the possible opening of a band-gap \cite{54}.

Epitaxial growth of hBN behaves in many ways similarly to that of graphene. The most widely used way to obtain hBN is by thermal decomposition of borazine (B₃H₆N₃) on transition metals; the surface properties of hBN are again dictated by the metal underneath \cite{56}. Here too, lattice mismatch between the hBN and the metal substrate leads to moiré pattern as shown in figure 1(b). In hBN-metal systems the region of strong interaction is limited to the sites where the N-atoms are on the top of the metal surface atoms. For other adsorption sites of the B and N atoms (i.e., TOP-FCC or HCP-FCC) the hBN-metal interaction is weak. Thus, the moiré of hBN on metals is characterized by periodically arranged, interacting ‘pore’ areas separated by connected regions of almost free-standing ‘wires’. The terminology of pores and wires stems from historical reasons \cite{57}; nevertheless, the hBN layer forms a full, atomically perfect layer without holes or other defects. The moiré topography is in contrast to graphene where connected valley sites separate isolated, periodic TOP sites \cite{58} (compare figure 1(a) to (b)). The corrugation of the hBN ‘nanomesh’ varies from metal to metal. If the mean hBN-metal distance is comparable to interlayer distance in bulk boron-nitride (\sim 3.33 \text{ Å}) as in the case of epitaxial hBN on Ir(111), Pt(111), or Cu(111), the topographic corrugation is small (e.g., \sim 0.35 \text{ Å} for hBN/Ir \cite{55, 59, 60}. For hBN grown on Ru(0001) or Rh(111) the minimum hBN-metal height is low (\sim 2.5 \text{ Å}) and the resulting corrugation is quite high (\sim 1 \text{ Å}) \cite{61, 62}. Irrespective of the supporting bulk metal, hBN shows a high electronic corrugation over the period of the moiré resulting in a significant difference in the local work function between the wire and pore sites (\sim 0.5eV for hBN on Rh(111), Ru(0001) or, Ir(111) and, \sim 0.3 eV for hBN/Cu(111) \cite{56}.

While the bulk support can have an effect on the properties of graphene and hBN, they are otherwise chemically relatively inert. Thus, molecules deposited on them interact with the 2D surface primarily through weak, vdW or \pi – \pi interactions. This makes these surfaces quite attractive for studying the fundamentals of supramolecular self-organization. We will go through self-assembly on 2D materials in detail in the next section.

3. Molecular assembly on 2D materials

Control over the strength of the molecule–substrate interaction and its spatial variation is the key to tuning the molecular adsorption patterns. If the molecule–substrate interactions are weaker than the intermolecular attraction, a close-packed islands of molecules will be observed also on non-smooth surfaces. On the other hand, stronger site-specific molecule–substrate interaction leads to site-selective adsorption.

3.1. Site-selective adsorption

First we will focus on the site-selective adsorption on strongly interacting G/Ru(0001) surface where the moiré pattern plays an active role in the assembly formation. Self-assembly of free-base phthalocyanine (H₂Pc) \cite{63, 64}, iron phthalocyanine (FePc) \cite{65–66}, nickel phthalocyanine (NiPc) \cite{63, 64}, manganese phthalocyanine (MnPc) \cite{64}, pentacene \cite{65, 67}, perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) \cite{68, 69}, tetracyanoquinodimethane (TCNQ) \cite{70, 71} and fullerene (C₆₀) \cite{72, 73} have been studied on this surface. At lower coverage, individual metal phthalocyanine (MPC) molecules occupy FCC region of the moiré. As the molecular coverage is increased, the molecules begin to occupy edges of the TOP region instead of HCP region. For a certain coverage, this results in the formation of a Kagome lattice, where the TOP sites still remain unoccupied while the FCC and HCP sites are occupied. The coverage dependent assembly has been studied by Gao and coworkers \cite{63, 65} for FePc molecules (shown in figures 2(a)–(c)). Other examples include H₂Pc, NiPc, FePc, MnPc molecules on G/Ru surface \cite{63, 64} which were shown to also form a Kagome lattice for right coverage.

Zhang et al \cite{65} studied molecular self-assembly of FePc and pentacene molecules on G/Ru(0001). Ab initio calculations suggest that the in-plane surface dipole (due to the work function modulation within the moiré unit cell) exists around the edge of the TOP region with the largest values along the TOP-FCC direction of the moiré. Therefore, molecules having significant polarizability tend to adsorb preferentially at FCC site. The enhanced stabilization of the molecules is the result of the interaction between the induced dipole moment of the molecule and the in-plane surface dipole \cite{76}. A large electric field in FCC-TOP direction due to the surface dipole is confirmed by the fact that pentacene molecules adsorb exclusively along this direction at low coverage \cite{67}. Density functional theory (DFT) calculations including vdW interactions demonstrated that the adsorption energy of the molecule was highest in this configuration. Increased deposition leads to sequential filling up of all FCC positions followed by the filling of the HCP sites—the TOP regions remain unoccupied even at high coverage of 0.7 monolayer (ML). A site-dependence of the adsorption energy is also at the heart of hierarchical adsorption of C₆₀ molecules on G/Ru(0001).
Unlike the previously described molecules, the bucky-balls start by populating the HCP valley sites to form heptamers before continuing onto the FCC sites and finally onto the TOP sites. A combination of decreasing adsorption energy and decreasing amount of charge transferred to C60 from HCP to the TOP sites, as indicated by DFT calculations, was suggested as a reason for the hierarchical growth.

TCNQ molecules deposited on G/Ru(0001) also show site-selective adsorption [70, 71]. Here, the adsorption mechanism is different from the dipole mediated adsorption as discussed earlier. TCNQ is known to be a strong electron acceptor with an electron affinity (EA) of 2.8 eV [77]. Therefore, such molecules tend to adsorb at the sites with higher electron density and lower work function [70] i.e., the HCP and FCC region compared to the TOP region. It is also possible that higher reactivity of the FCC/HCP sites compared to the TOP regions contributes to the patterned assembly. At slightly higher coverage all the FCC and HCP regions are covered while the TOP regions stay unoccupied creating a Kagome lattice. At full monolayer coverage the molecules occupy the TOP region as well. The coverage dependent site-selective adsorption is shown in figures 2(d)–(f).

Molecular self-assemblies on epitaxial hBN layer grown on metal surfaces also exhibit site-selectivity due to the presence of a moiré pattern. The presence of a
A number of molecules such as C_{60} are appealing substrates for templated molecular assembly. The work function across the hBN moiré also makes it a significant geometric corrugation and periodic modulation of the work function across the hBN moiré also makes it an appealing substrate for templated molecular assembly. A number of molecules such as C_{60} [57], naphthalocyanine [81], CuPc [62, 78], H_{2}Pc [78], CoPc [79], H_{3}Pc [80], 5,5″,5″,5‴-hexaiodocyclohexa-m-phenylene (I_{6}CHP) [82], and TCNQ [80] selectively adsorb on the pores of the hBN surface. Similar to the case of G/Ru(0001), the adsorption mechanism is related to the presence of in-plane electric field due to the strong work function modulation, which results in trapping the molecules in the pores [62, 78].

In epitaxial hBN, the maximum potential gradient exists at the edge of the pore (up to 1 V nm^{-1}) causing the molecules to adsorb there (figures 3(a), (b)). CoPc on hBN/Ir(111) [79] and I_{6}CHP [82], H_{2}Pc, and CuPc on hBN/Rh(111) [78] are examples of such off-center adsorption. Aggregates of small molecules such as porphine and TCNQ on long-period hBN moiré on Cu(111) (periodicity 12 nm) nucleate at the pore site for low coverages [80]. A similar observation has been made for Xe atoms on hBN/Rh(111) surface [62, 83].

On systems with a shorter moiré period, preferential adsorption in the pore regions disturb the long-range order of the molecular layer. For example, deposition of nearly a full-monolayer of CoPc on hBN/Ir(111) results in short range order with a close-packed square lattice [79]. However, there is no long range order due to the strong molecule–substrate interactions in the pores of the hBN moiré on Ir(111) and the mismatch in the preferred nearest-neighbor distance in the molecular layer and the moiré period.

While free-base porphine (2H-P) exhibits site-selective adsorption on hBN/Cu(111) surface [80] as shown in the figure 3(c), it is possible to tailor the intermolecular interactions by adding terminal groups to porphine molecules resulting in the loss of site-selectivity. Carbonitrile-functionalized porphyrin molecules (2H-TPCN) deposited on hBN/Cu(111) [84] show close-packed islands, because non-covalent intermolecular attraction (due to the presence of terminal cyano-bi-phenylene groups) dominates over the molecule–substrate interaction.

3.2. Close-packed assembly

Site-selectivity is not expected on weakly interacting systems, where the work function modulation and the geometric corrugation across the moiré unit cell are small [85–87]. Precisely this has been observed for TCNQ [88] and MPC molecules (e.g. CoPc [74, 89], CuPc [74], and F_{16}CoPc [74]) on G/Ir(111). An example of CoPc on G/Ir(111) is shown in figure 2(g). While the work function modulation and geometrical corrugation are too small to dictate the assembly of molecules, their unit cell can differ slightly from ideal square packing [89]. Close-packed molecular islands with the exact geometry being determined by the shape of the molecule is also observed on other weakly interacting metal-graphene systems e.g., square lattice of FePc on G/Pt(111) [64], F_{16}CuPc on G/SiC [90], CoPc on G/hBN [91] and hexagonal packing of C_{60} on G/Cu(111) [92] and G/SiC [93, 94]. Larger substrate corrugation can affect the lattice quality and domain size as demonstrated by CoPc self-assembly on G/SiO_{2} and G/hBN. While CoPc forms a square lattice on both substrates, on G/SiO_{2} the domain size is limited and there is disorder in the molecular ordering within the domains. On the geometrically smooth G/hBN substrate, the domain size is only limited by the size of the terraces of the underlying hBN [91].

![Figure 3. Site-selective assembly on hBN. (a) CuPc molecules adsorb preferentially on the pore site of hBN/Rh(111) nanomesh. (b) CoPc molecules preferentially adsorb on the pore sites of hBN/Ir(111) moiré. (c) Extended self-assembled 2H-P islands form on hBN/Cu(111) confined to certain areas of the moiré. The moiré unit cell is shown by the white rhombus. The islands can merge to form a continuous monolayer as seen in the bottom-right corner. Adapted with permission from [78–80].]
On weakly interacting graphene stronger intermolecular interactions affect the self-assembly profoundly, e.g., PTCDA on G/Ru(111) [95] and G/SiC [96–99], and PCTDI (perylene tetra-carboxylic di-imide) on G/SiC [100] assemble in close-packed herringbone structures to maximize intermolecular hydrogen bonds (C-H…O and N-H…O, respectively). Additionally, the close-packed islands of PTCDA [97] and PCTDI [100] were observed to grow uninterrupted over step-edges and defects in the underlying graphene. These studies observed growth of multiple domains which were not aligned to the high-symmetry directions of graphene. These observations indicate that the molecular assembly on weakly coupled graphene is dictated by intermolecular interactions (vdW or hydrogen bonding) rather than molecule–substrate interactions.

In the case of graphene deposited on insulating substrates, the reduced screening can have an effect on the molecular self-assembly. This was demonstrated by Tsai et al., who showed that F4TCNQ on G/hBN forms close-packed islands at sufficiently high coverages [75] (figures 2(h), (i)). The molecules pack in a head-to-tail fashion in compact islands, in contrast to F4TCNQ on epitaxial G/Ru(0001) or G/Ir(111), where site-selectivity causes a staggered assembly [88, 101].

Interestingly, close-packed assemblies at sub-monolayer coverage can be formed even on the surface of strongly corrugated graphene by post-deposition annealing. On the G/Ru(0001) surface, PTCDA has been observed to assemble into a herringbone arrangement with only some of the TOP sites remaining empty after heating the substrate [68]. Similarly, pentacene [67] and C60 [73] assemble into close-packed structures on G/Ru(0001) under high temperature deposition and annealing after deposition, respectively. The higher temperature causes the molecules to be mobile, facilitating their assembly into a close-packed, ordered structures corresponding to a higher adsorption energy per unit area.

### 3.3. Assembly engineering

It is possible to tailor molecular self-assembly by controlling the molecule–substrate interactions even on the strongly corrugated G/Ru(0001) surface. Yang et al. [64] demonstrated that for comparable coverage, a stronger (FePc), intermediate (MnPc), and weaker (NiPc and H2Pc) molecule–substrate interactions lead to selective adsorption at FCC sites only, molecular chains in the valley regions, and a Kagome lattice, respectively. The molecule–substrate interaction can further be changed through metal intercalation under the otherwise weakly interacting G/Ir(111). The intercalation of Co and Fe leads to an enhancement of the moiré corrugation (from ~50 pm to ~120–150 pm) and chemical binding between graphene and the substrate resulting in increased molecule–substrate interactions [102, 103]. Bazarnik et al. [104] demonstrated that for low temperature deposition and at low coverages both CoPc and CuPc form one-dimensional molecular chains in the lower lying region of the moiré formed on Fe (or Co) intercalated G/Ir(111). At a slightly higher coverage, the molecules begin to form hexagonal rings around the TOP region as shown in figure 4(a). For room temperature deposition at a higher coverage, the molecules assemble into slightly distorted honeycomb lattices with empty TOP sites. Interestingly, when the periodicity of the moiré increases due to intercalation of a different rotational domain of G/Ir(111), the assembled structure changes too. For intercalated graphene with a periodicity of 2.85 nm, the honeycomb lattice transforms into a Kagome lattice. An STM image of this assembly is shown in figure 4(b).

Further, self-assembled structures can also be modified by tuning intermolecular interactions on a given surface. For assemblies stabilized by directional hydrogen bonds between the molecules, tuning the location of the electronegative species in the molecule can lead to completely different assembly. An example of this behavior is the assembly of 2,4′-bis(terpyridine) (2,4′-BTP) [105] and 3,3′-bis(terpyridine) (3,3′-BTP) [68] on G/Ru. The molecule 2,4′-BTP assembles exclusively into linear, parallel chains lying along the symmetry axis of graphene (figure 4(c)); on the other hand, 3,3′-BTP forms rings and short chains centered around the TOP site (figure 4(d)). In both cases, adjacent molecules are seen to lie in an anti-parallel fashion, indicating the formation of C-H…N hydrogen bonds. Such disparity in the assembly is simply due to the difference in the position of the nitrogen atoms in these two molecules.

### 3.3. Molecular templates

The templating effect of graphene and hBN is not confined to a monolayer of molecules. 2nd layer of C60 molecules deposited on G/Ru(0001) surface shows highly ordered assembly following the corrugation of the moiré pattern shown in figures 5(a), (b). However, the 3rd layer is no longer corrugated and reaches the bulk structure of C60 as shown in figure 5(c) [72]. As another example, the molecules of the second layer of CoPc on hBN/Ir(111) align themselves with the pores of the underlying moiré pattern [79].

Multi-layer growth on weakly coupled graphene is dependent on the adsorption motif of the first adlayer. As mentioned in section 3.1, PTCDA on G/SiC assembles in a herringbone pattern. The molecules in 2nd and 3rd layer mimic the herringbone arrangement of the first layer [96]. For pentacene, on the other hand, although the first layer of molecules lie flat with their long-axis aligned along the graphene zigzag direction, the second layer prefers to stand upright in a herringbone fashion [108] similar to on HOPG [109].

Molecular assembly with porous networks have often been used as a template to steer the assembly of other molecular species [2, 3]. Similar assemblies have been replicated on weakly coupled graphene to obtain nano-porous networks and use them in the so-called ‘host-guest’ architectures. For example, sequential deposition of PTCDA and the 3-fold symmetric molecule melamine has been used to form hexagonal network stabilized by intermolecular hydrogen bonds on G/SiC [110]. Hexagonal porous network stabilized by hydrogen bonds have also been realized by 3-fold symmetric tricarbonylic acids e.g., trimesic acid (TMA) and
benzene-tribenzoic acid (BTB), which have been studied in detail on graphite and noble metal surfaces [111]. In a comparative study of TMA assembly at the liquid-solid interface on G/SiC and graphite, the molecules were observed to assemble into a hexagonal network with a periodicity of ~1.6 nm and identical epitaxy on both surfaces [112]. In another study carried out at the solid-liquid interface on exfoliated graphene on silicon dioxide [106], deposition of TMA resulted in a close-packed structure. On subsequent deposition of coronene, the assembly changes to a honeycomb arrangement of TMA (periodicity ≈1.7 nm) with the coronene occupying the pores, as shown in figure 5(d). This is an interesting example of the incorporation of the guest molecule causing a phase-change of the host network.

After deposition in UHV, 1,3,5-benzenetribenzoic acid (BTB) assemblies into an extended hexagonal mesh with a periodicity of ~3.2 nm on G/Ir(111) [107]. The network is quite stable and robust (figure 5(e)) with an estimated bonding energy of 1.95 eV per molecule, extending for hundreds of nanometers over step-edges of the underlying substrate. The periodic pores of the nanomesh can be used to pattern molecular assembly as demonstrated with CoPc. Remarkably two CoPcs could be hosted in a single pore without destroying the network—the strong yet flexible hydrogen bonds holding the network together undergo stretching to accommodate the guest molecules. When all pores of the BTB network are uniformly occupied with two CoPcs, the guest molecules are seen to arrange in a herringbone pattern as shown in figure 5(f). The formation of the herringbone pattern is driven by the reduction of the energy cost associated with stretching and twisting the hydrogen bonds between the BTB molecules.

3.5. Covalently bonded structures

Several different coupling mechanisms for obtaining covalently bonded molecular assemblies have been demonstrated on metal single crystal substrates, where the catalytic activity of the metal substrate is important. One of the better studied mechanisms is Ullmann-type coupling, where first a halogen

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Figure 4. Assembly engineering. (a) CoPc molecules form a honeycomb lattice on G/Ir(111) intercalated with Co. Here the moiré periodicity is same as that of pristine G/Ir. (b) On G/Co/Ir(111) surface with larger moiré periodicity (2.85 nm compare to ~2.5 nm), the structure changes to a Kagome lattice [104]. (c) 2,4′-BTP molecules form long parallel chains along the symmetry direction of G/Ru(0001) [105]. (d) 3,3′-BTP molecules form rings and short chains on the surface [68]. The difference comes from the different position of the N atoms on the isostructural molecules which modifies the directional hydrogen bonding. Adapted with permission from [68, 104, 105].
—carbon bond in a precursor is cleaved, and the resulting radicals react to form carbon-carbon bonds [113–116]. This has been used to carry out on-surface polymerization [115, 117], and in particular, synthesize atomically well-defined graphene nanoribbons of different widths and edge terminations [116, 118–123]. Finally, it was very recently demonstrated that on-surface covalent coupling can be used to laterally anchor organic heteromolecules to graphene nanostructures through covalent bonds [124].

The difficulties in using the radical coupling on surfaces other than bulk metals are highlighted by Dienel et al [82]. They describe the reactivity of 5,5′,5″,5‴-hexabiodocyclohexa-m-phenylene (I₆CHP) on hBN/Ru(0001) (figures 6(a)–(c)). I₆CHP is typically very reactive on metal surfaces and dissociates all its iodine atoms on Cu(111), Ag(111), and even Au(111) already at room temperature [125]. The situation is different on hBN-covered metal surface as shown in figure 6(a), where it can be seen that following deposition at room-temperature, I₆CHP remains undissociated. The reactivity of the I₆CHP was tested using voltage pulses from the tip of the STM as shown in figure 6(b). These experiments showed that the iodine atoms dissociate at alternating positions around the molecule and not more than three iodine atoms can be removed. The formed radicals are immediately stabilized by a bond formation of the radical site with the underlying boron atom [126]. This locks the molecule in position and consequently favors the remaining alternating sites for dehalogenation.

Dehalogenation can also be induced by thermal annealing [82]. Mild annealing (up to 550 K for 20 min) again results at most three iodines being cleaved (figure 6(c) (left panel)). After annealing to even higher temperatures (800 and 850 K for 30 min, middle and right panels of figure 6(c)), more iodine atoms can be removed. Only at annealing temperatures of 850 K was it possible to produce iodine-free oligomers. However, the resulting structures do not yield the long-range order that can be observed on metal substrates after similar annealing [125]. On metal surfaces, the radicals are stabilized by bonding with the substrate, while the precursor molecules can still retain sufficient mobility to yield high quality structures.

Dehalogenation with brominated precursor molecule 1,3,5-tris(4-bromophenyl)-benzene (TBB) on hBN and graphene on Ni(111) has also been attempted [127]. Annealing the sample to 520–570 K results in debromination of the precursor molecules, which subsequently form covalently bound assemblies. However, these lack long range order observed with the same precursor molecules on coinage metals. Similar to I₆CHP, limited mobility of the dehalogenated molecules due to a strong interaction with the hBN and
graphene surfaces is likely to be responsible for the lack of long-range order. The strong interaction was further substantiated by DFT calculations showing a strong interaction between the phenyl unit and G/Ni(111) [127]. Finally, the authors argue that the order and spatial extension of the cross-linked molecules can be improved by a suitable choice of supporting metal surface for graphene and hBN, which would be more weakly interacting than Ni(111).

In contrast to the covalently bonded assemblies, metal coordination bonds have been demonstrated to yield molecular assemblies with long-range order on non-reactive hBN [84]. Urgel and co-workers investigated carbonitrile-functionalized porphyrin derivatives (2H-TPCN) cross-linked with Co atoms on epitaxial hBN on Cu(111) (figures 6(d), (e)). Here, the molecule self-assembles into a densely packed layer with a square unit cell. After evaporation of cobalt atoms onto the substrate at room temperature, metalation of the porphyrins is observed i.e., Co-TPCN is formed. Coordination networks can be formed once submonolayer coverages of TPCN is exposed to Co atoms at 350 K [84]. Two different packing schemes are formed at this temperature: a densely packed array representing the pure molecular phase and a network structure exhibiting a larger square unit cell and a central protrusion (blue square in figure 6(e)); the latter structure was assigned to a Co-directed assembly of a metal-organic coordination network. Surprisingly, they have 4-fold coordination in contrast to what is observed on metal substrates.

Single-molecule reactions have also been investigated, for example, dehydrogenation of H2Pc on G/Ir(111) [128]. In this particular case, graphene was used as an inert substrate that does not participate in the removal of the inner core hydrogens. Importantly, the formed radical did not bond with the underlying graphene, which allowed the study of the molecule in the same adsorption geometry before and after dehydrogenation. Another single molecule reaction was demonstrated by a novel cycloaddition scheme between various phthalocyanines and G/Ir(111) [129]. This reaction could be driven reversibly by voltage pulses from the tip of a low-temperature STM. The reaction only occurs on a certain part of the graphene moiré pattern on Ir(111), which suggests that the bonding of the graphene with the underlying Ir(111) results in dangling bonds on the graphene surface.

4. Tunneling spectroscopy on 2D materials

Molecules physisorbed on a surface through vdW interactions retain their gas-phase electronic properties. This is no longer the case for molecules adsorbing through strong chemical bonds (e.g. covalent, metallic, and ionic bonds) [130]. An extensive review on molecule-metal bonds has been provided by Nilsson et al [131]. Molecular orbitals of molecules adsorbed on metal surfaces are strongly hybridized (resulting in broadening, shifting, and mixing of the orbitals) because of the interaction with the continuum of electronic states in the metal [130, 132]. Typically, the spectroscopic signatures of the molecular orbitals are too broad to be reliably detected [132]. Molecules can be electronically decoupled from the metal substrate by the use of ultrathin insulating films that

Figure 6. Covalent reactions on 2D materials. (a) L6CHP adsorption on hBN on Rh(111). (b) Step-by-step dehalogenation of a single L6CHP induced by voltage pulses from the STM tip. (c) Dehalogenation and subsequent cross-linking following thermal annealing to 550 K (left), 800 K (middle) and 850 K (right) [82]. (d) Schematic showing two ways of metal complexation of 2H-TPCN. At room temperature the Co atoms go to the tetrapyrole pocket whereas on annealing to 350 K they coordinate to the –CN peripheral groups yielding a metal-organic coordination network. (e) Structure (left) and small-scale STM image (right) of the metallo-supramolecular network [84]. Adapted with permission from [82, 84].
allow combining insulating surfaces and STM. The insulating layer (∼few Å) can still be sufficiently thin to allow STM operation without difficulties. Ultrathin layers of conventional insulating materials, for example, alkali-halides [133–135], metal-oxides [76, 136–138], metal-nitrides [139, 140], passivated semiconductors [141, 142] have been used to study the properties of single atoms and molecules, and various aspects of molecular electronics in general.

The decoupling makes it possible to study molecules whose properties closely match those found in the gas phase (e.g., magnetic moment [143], fluorescence [136]). In a seminal experiment, Repp et al. [133] demonstrated that a NaCl bilayer is sufficient to electronically decouple pentacene molecules from the underlying Cu(111) surface. STS on the molecule shows sharp resonances in the differential conductance (dI/dV) spectra corresponding to temporary electron addition (positive sample bias) and electron removal (negative sample bias) to/from the molecule. These peaks are also termed positive (PIR) and negative ion resonances (NIR) referring to the transient occupation of the molecular orbitals [133, 144]. The first PIR at negative and the first NIR peak at positive bias correspond to the electron tunneling through the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule, respectively. While these peaks are often referred to HOMO and LUMO, energy difference between the PIR and NIR is not equal to the HOMO–LUMO gap. This so-called transport gap is larger than the HOMO–LUMO gap due to the Coulomb charging energies associated with adding/removing electrons to/from the molecule [145, 146]. It is more correct to think of PIR and NIR as corresponding to the ionization potential (IP) and the EA of the molecule, respectively (see [147–150] for details).

The very exciting aspect of STM is that it allows—in addition to measuring the energy positions of the molecular resonances—mapping out the molecular orbitals in real space. STM topographic images at bias values of PIR and NIR on a molecule deposited on a decoupling layer resemble the HOMO and the LUMO orbitals of gas phase molecule as shown by Repp et al. [133]. These orbitals can be imaged with very high spatial resolution, especially using molecular modified tips [133, 135, 151].

4.1. Orbital decoupling and orbital imaging on 2D materials

Similar to the above mentioned insulating layers, epitaxial graphene and hBN are also able to efficiently decouple the molecules from the underlying metal substrates by virtue of their chemical inertness and low density of states around the Fermi level. They can be used as a supporting surface to study the properties of single atoms and molecules for various aspects of molecular electronics. Experiments on C80 [92, 93], TCNQ [70], Molecules [74, 152], and PTCDAs 69, 95, 96 adsorbed on epitaxial graphene indicate that molecules do indeed retain their intrinsic properties. Järvinen et al. [74] have carried out STS and orbital imaging of CuPc, CoPc and F4bCoPc molecules deposited on G/Ir(111). The dI/dV spectra displaying the HOMO and LUMO resonances are shown in figure 7(a). The value of the transport gap (HOMO–LUMO gap measured on G/Ir(111)) should be smaller than in thick molecular films due to the additional screening from the graphene and the underlying metal substrate. As mentioned above, imaging at the bias voltages corresponding to the molecular resonances can be used to study the molecular orbital structure of each of the molecules. Figures 7(b), (c) shows HOMO and LUMO images of CoPc which closely resemble the DFT calculated orbitals for the gas-phase molecule. The HOMO orbital is delocalized over the π system of the carbon backbone while the LUMO orbital is localized on the central Co atom.

Similarly, Martínez-Galera et al. [95] demonstrated that graphene decouples PTCDAs molecules from Pt(111) surface, as shown in figures 7(e), (f). Here too, HOMO and LUMO orbital images closely resemble the respective calculated orbital images for an isolated molecule. Zheng et al. [153] observed that the transport gap of PTCDAs molecule increases from Au(111) (3.1 eV) to HOPG (3.5 eV) to semi-conducting WS2 (3.7 eV) surface. These observations were substantiated using DFT calculations that take image charges at the substrate into account; this highlights the importance of substrate-induced screening in STM studies of single molecules. Cho et al. [93] studied C60 molecules deposited on G/SiC surfaces, which show three peaks at −2.7, 0.8, and 1.6 V. These features are likely to correspond to HOMO, LUMO, and LUMO +1; again, the HOMO–LUMO gap of 3.5 eV is higher than on Au(111) surface (2.7 eV [154]). A number of UHV-based non-STM studies have also been carried out to discuss the decoupling of molecules due to epitaxial graphene layer [152, 155–157].

As discussed above, molecules adsorbed on epitaxial graphene are weakly coupled to the substrate and retain their intrinsic properties. The same is true for graphene deposited on an insulator e.g., SiO2 or hBN. CoPc molecules deposited on these substrates show life-time limited lorentzian line-shapes [91]. Graphene on insulating substrate makes it possible to tune the charge carrier concentration through external doping. Voltage on the back gate shifts the graphene Fermi level w.r.t. the Dirac point and hence, the molecular resonances also shift. Riss et al. demonstrated STM measurements with a gate electrode by performing experiments on 1,3,5-tris-(2,2-dicyanovinyl)benzene (CVB) molecules on a G/hBN substrate [158]. They showed that the molecular resonances could be shifted by ca. 200 mV by sweeping the gate voltage from 0 to 60 V. This suggests controlling charging in single molecules and molecular assemblies while simultaneously imaging their orbitals with sub-molecular spatial resolution.

In two separate reports, Schulz et al. [79] and Joshi et al. [80] have shown that CoPc molecules deposited on hBN/Ir(111) surface and 2H-P molecules deposited on hBN/Cu(111) surface are also decoupled from the metal surfaces due to the epitaxial hBN layer. Figure 7(d) shows HOMO (−1.1 V) and LUMO (0.8 V) peaks in the STS spectra recorded on CoPc molecules adsorbed on the wire region of the hBN moiré and the STM images recorded at the corresponding bias voltages. These sharp resonances have life-time limited lorentzian shape and enable high energy
resolution spectroscopy of isolated molecules [79, 159]. Similarly, sharp HOMO and LUMO peaks were observed for the 2H-P molecules on the hBN/Cu(111) surface [80]. Finally, the presence of work function modulation over the moiré of hBN on metal surface leads to site-selective charging of the molecules which will be discussed in the next section.

4.2. Site-selective gating and charging

We have discussed site-selective adsorption of molecules on 2D materials which is related to periodic modulation of electronic and chemical properties across the moiré pattern. This also results in a modulation of molecular orbitals of the molecules and in some cases, to site-selective charging of molecules. Already on a weakly interacting system, G/Ir(111), Järvinen et al [74] observed that the LUMO resonance peak of CoPc and F₁₆CoPc is modulated by as much as 200 mV across the moiré. The molecules adsorbed on the TOP region of the moiré showed the LUMO peak at higher energy in line with the fact that the TOP region has a larger work function. However, the HOMO did not shift as much, i.e. the HOMO–LUMO gap is increased on the TOP region. Thus the rigid shift due to work function difference (estimated 60 meV across the moiré) alone is not sufficient to explain these orbital shifts. Other possible explanation are a change in the screening due to modulation of graphene—Ir(111) distance across the moiré, modulation of bonding character of graphene across the moiré, and spatially different symmetry of molecular resonances.

Compared to G/Ir(111), epitaxial hBN on different metals exhibits stronger work function modulation and geometric corrugation across moiré pattern, which would be expected to lead to more drastic effects on the orbital energies. A number of molecules deposited on different hBN surfaces [79, 80, 84, 160] show such site-specific modulation of molecular orbitals. Therefore, many interesting physical effects become visible. Joshi et al [80] report modulation of the position of the molecular orbitals and the HOMO–LUMO

[Figure 7. Molecular orbital imaging. (a) dI/dV spectra of CoPc, CuPc, and F₁₆CoPc molecules on G/Ir(111) recorded at the center and arm of the molecules. Peaks at positive and negative bias correspond to tunneling into the LUMO and HOMO, respectively. (b), (c) STM images of CoPc assembly recorded showing the LUMO (b) and the HOMO (c). Scale bars are 3 nm [74]. (d) STS recorded on a CoPc molecule adsorbed on the wire site of hBN/Ir(111) moiré. Insets show STM images at −1.2 and 0.8 V resembling HOMO and LUMO orbitals, respectively. Peak at 1.9 V corresponds to tunneling into LUMO+1 orbital [79]. (e) dI/dV spectrum of PTCDA molecules on G/Pt(111) showing HOMO and LUMO resonances. (f) STM images recorded at 1.34 V and −2.3 V show the LUMO and HOMO, respectively. Calculated orbitals are shown in the insets [95]. Adapted with permission from [74, 79, 95].]
gap across the moiré of hBN/Cu(111). Figure 8(a) shows dI/dV spectra recorded on 2H-P molecules adsorbed on different sites of the moiré. The LUMO peak is shifted up by as much as 300 mV for the molecules lying on the bridge compared to the pore site. This shift is smaller for the molecules lying on the rim of the moiré. The shift of the LUMO matches the work function difference between the pore and the bridge site (~300 meV), indicating that the change in the orbital energy simply reflects the local vacuum level alignment. However, the HOMO–LUMO gap was also found to be modulated with respect to the moiré as shown in figure 8(a). The smallest gap is observed for the molecules on the pore region. Here too, charge screening has to be taken into account to explain the shifts. The energy shift of the LUMO orbital is also observed in the bias dependent STM imaging as shown in figure 8(b). The molecules on the pore region have lowest lying LUMO and appear bright first in STM images. LUMO orbitals of other molecules get inside the bias window as the sample bias is increased and subsequently at 1.65 V, the whole monolayer has similar brightness. These results are not particular to 2H-P; 2H-TPCN and Co-TPCN molecules [84] adsorbed on on hBN/Cu(111) show similar modulation of LUMO peak and HOMO–LUMO gap.

The effect of work function modulation across moiré is even stronger for CoPc molecules adsorbed on hBN/Ir(111) surface. Schulz et al. [79] performed STS on CoPc molecules adsorbed on the pore and on wire site of the moiré. While the molecules on the wire site (see figure 7(d)) show peaks at −1.1 V (HOMO), 0.8 V (LUMO) and 1.7 V (LUMO+1), the molecules on pore site shows a strong peak at −0.4 V as shown in figure 8(c). Bias dependent STM imaging show different orbitals participating at different biases. Black rhombus shows the unit cell of hBN/Ir(111) moiré. While the molecules at the pore resemble LUMO, at the wire site they resemble HOMO at −1.2 V. As the bias is increased to 0.8 V and further to 1.2 V, the molecules at the wire site resemble LUMO and the molecules at the pore site resemble higher order orbitals [79]. Adapted with permission from [79, 80].
molecule, the peak is attributed to the LUMO shifted below the Fermi level due to electron transfer from the substrate to the molecule. Work function of pore site is smaller by 0.5 eV from the wire regions—this is sufficient to induce charging. The spectra recorded on the lobes of the charged molecule display additional resonances that cannot be explained within the simple single-particle picture [159]. Instead, the results can be understood as a series of many-body excitations of the different charge states of the molecule. These results rely on the possibility of carrying out high-resolution STS and the fact that different charge states of the same molecule can be probed in chemically equivalent environment, which are made possible by the hBN insulating film.

The decoupling by hBN results in sufficiently narrow widths of the molecular resonances and vibronic features in the spectra are easily resolved. The vibronic results reflect from elastic tunneling through one of the molecular resonances while simultaneously exciting a molecular vibration [161, 162], which manifests as satellite peaks around that molecular resonance peak with a spacing determined by the energy of vibrational mode that is excited [163–165]. The vibronic progressions of LUMO orbitals of CoPC molecules on the wire and pore sites of the moiré formed by hBN/Ir(111) are evident in figures 7(d) and 8(c) [79].

4.3. Tip-gated charging

Molecules adsorbed on thin insulating layers probed by STM constitute a double-barrier tunnel junction due to the finite polarizability of the insulating layer. In such junctions, a part of the voltage applied between the STM tip and the substrate drops between the molecule and the substrate—a lever-arm effect. The ratio of the voltage drop across the tip-molecule and tip-substrate junctions depends on their respective capacitances and is called the lever-arm factor (denoted by α). The ratio (0 < α < 1) can be tuned by moving the tip towards or away from the surface. Tunneling through a double-barrier junction can give rise to charging when a molecular orbital close to the Fermi level of the substrate crosses the Fermi level due to finite voltage drop across the insulating layer [166] (schematic in figures 9(a), (b)). The charging results in a modification of the potential barrier profile of the junction [167] and subsequently results in a sharp change in the df/dV spectrum. Ho and his group used ultrathin Al2O3 layer on NiAl substrate to create the double-barrier junction and investigated tip-gated charging of the molecules. This effect is also known as bipolar tunneling [161].

Liu et al shows this can be observed with MnPc molecules adsorbed on hBN/Rh(111) [160]. One of the adsorption sites across the moiré shows the molecules with a bright center in a neutral state but having their HOMO level close (∼100 meV) to the Fermi energy (shown by yellow arrow in figure 9(c)). This orbital is brought above the Fermi energy at positive bias and a sharp peak (indicated with asterisk) appears in df/dV spectrum along with LUMO orbital of the molecule. The bias voltage corresponding to the charging peak depends on: (i) the exact location of the HOMO, (ii) the location of the STM tip, and (iii) the relative potential drop across the tip-molecule and molecule-substrate junctions (lever-arm factor). Figure 9(d) shows stacked df/dV spectra recorded across the molecule with a topographic image shown in the inset. The locus of the charging peak (large df/dV feature) seems to follow parabolic arc along the bright spot at the center, which corresponds to the LUMO of the molecule. Above the parabola, the molecule is in the charged state and below it is neutral. The locus of the charging peak depends on the tip geometry as it is determined by the electrostatic potential distribution over the tip-substrate gap. Further, by changing the set-point current, value of lever-arm factor can be varied which changes the position of the charging peak.

Tip-gated charging has also been demonstrated for F2TCNQ molecules adsorbed on the surface of a back-gated graphene device (graphene on hBN) [168]. Here, the position of the LUMO of the molecule with respect to the Fermi-level of the substrate can be precisely controlled and this tunes the position of the sharp charging peaks in the df/dV spectra. In addition, the authors observe a non-rigid shift of the LUMO energy w.r.t the Dirac point that is attributed to graphene polarization effects.

5. Band structure engineering and doping of graphene

The electronic properties of monolayer graphene are described by its conical band structure at the K and K’-points of the Brillouin zone. The linear dispersion of the charge carriers near the Dirac points gives graphene many of its fascinating electronic properties e.g., high electron mobility and ambipolar transport [169]. However, application of graphene in practical electronic devices has still not been realized as it requires two things: precise control over the type and concentration of charge-carriers and opening a sizeable band gap in the graphene band-structure [170]. Furthermore, these goals should be achieved through methods that are inexpensive and scalable and do not compromise the wonderful electronic properties of graphene. Many schemes have been used to introduce a band-gap in graphene. Quantum confinement of charge carriers in lithographically defined graphene nanostructures and unzipped carbon nanotubes can be used to create a band gap [171–176], but these methods cannot be used to achieve atomically well-defined nanoribbon edges. Bottom-up on-surface synthesis offer unprecedented control over the nanoribbon width and edge termination [116, 120, 122, 123]. However, contacting these very narrow ribbons is still a major technological challenge [177]. Recently, experiments on graphene on hBN devices have shown band gaps of up to 300 meV depending on the misalignment angle of the two lattices [178]. The exact mechanism of the gap opening is still under debate, with both breaking of the graphene sublattice symmetry due to the underlying hBN [178] and biaxial strain [179] have been proposed.

Covalent functionalization can also be used for both gap opening and doping and band gaps greater than an eV have been reached through partial rehybridization of the sp2 carbon
atoms to sp³ e.g., by hydrogen [17] or fluorine [180]. Substitutional doping with boron and nitrogen atoms to obtain hole (p-type) or electron (n-type) rich graphene has also been demonstrated [181–184]. However, these methods potentially disrupt the extended π-conjugation of graphene and lead to degradation of graphene’s exceptional electronic properties. On the other hand, physisorbed molecules interacting with graphene through weak vdW interactions are expected to offer a route to modify graphene’s electronic properties without degrading its desirable properties, even under high charge carrier density.

Doping of graphene by physisorbed molecules can be achieved easily by means of interfacial charge transfer, which can be tuned through the energy level alignment of the molecular frontier orbitals with respect to the Fermi level (\(E_F\), which is \(\approx 4.5\) eV with respect to the vacuum for free-standing graphene [185]) as shown in figure 10(a). If the EA of the molecule is larger than graphene work function, the molecule will accept electrons from graphene and make it hole-doped (i.e., p-doped). Conversely, if the IP of the molecule is smaller than graphene work function, the molecule will donate electrons to graphene, making it electron-doped (i.e., n-doped). The EA and IP of the molecule will be modified from their gas-phase values by screening due to the graphene surface. While DFT calculations including vdW corrections are the best available theoretical means to estimate the amount of charge transfer between a given molecule and the graphene surface [186–188], they can also be estimated based on photoelectron or Raman spectroscopy or by transport experiments. In addition to doping, periodic potential modulation has been proposed as means of breaking the sublattice symmetry in graphene [189]. An adlayer with the correct symmetry and period can potentially lead to a bandgap in graphene.

To date, many small gas molecules and hydrocarbons have been used to dope graphene with both donor (e.g., NH₃ [190], polyethyleneimine [191], naphthalenediamine, dimethylantracene [192]) and acceptor-type dopants (e.g., H₂O

**Figure 9.** Tip-gated charging. (a) Energy level diagram for neutral MnPc in STM junction depicting the formation of double-barrier tunnel junction. The HOMO (shown in blue) of the molecule is very close the Fermi level. (b) Energy level diagram corresponding to tip-gated charging of the MnPc molecule at positive sample bias, \(V_b\). Here, the HOMO crosses the Fermi level (shown in red) and the molecule loses an electron to form MnPc⁺. \(\alpha\) is the lever-arm factor. (c) \(dI/dV\) spectrum recorded on the lobe shows HOMO close to Fermi level (indicated by yellow arrow) and a sharp peak at positive bias (indicated by asterisk) corresponding to the tip-gated charging. Spectrum at the center of the molecule shows broad LUMO peak along with the charging peak. (d) Stacked \(dI/dV\) spectra taken across the molecule shows the locus of the charging peak and LUMO orbital. Adapted with permission from [160].
Figure 10. Charge donor and acceptors on graphene. (a) Schematic of doping of graphene by molecules: molecules with LUMO lying at energy lower than graphene Fermi level $E_F$ spontaneously accept electrons from graphene making the latter p-doped (right side). Conversely, molecules with the HOMO above graphene $E_F$ spontaneously donate electrons to graphene making the latter n-doped (left side) [21]. (b) Theoretical data points (black squares) on acceptors (TCNQ, $F_4$TCNQ), donors (TTF) and their salts on graphene. The abscissa gives change in $E_F$ and, ordinate gives change in work function of graphene after deposition of molecules [195]. (c) Raman measurements showing p-doping effect of OPA on graphene. Inset shows AFM image of OPA assembly on G/SiO$_2$ [196]. (d) ARPES data of (i) G/SiC ($E_F = -0.42$ eV) which is intrinsically n-doped, (ii) after deposition of 0.8 nm of $F_2$TCNQ on it ($E_F$ saturates at 0 eV) and, (iii) after deposition of 0.4 nm of TCNQ on it ($E_F$ saturates at $-0.25$ eV) [197]. (e) Electrical transport measurements on a G/SiO$_2$ FET before and after treatment with TMA indicating p-doping. Inset shows STM image of TMA assembly at solid–liquid interface on G/SiC. [106]. (f) $I_{DS}$ – $V_{DS}$ curves of G/SiO$_2$ FET before and after repeated cycles of treatment with OA indicating increased n-doping and improved mobility with each cycle. Inset shows STM image of OA assembly on HOPG [198]. Adapted with permission from [21, 106, 195–198].

[193]. O$_2$ [194], diazonium salts [191], pyrenetetralsulfonic acid, dibromoanthracene [192]. These have resulted in changes in the charge carrier density without degradation of electron mobility. Moreover, this type of doping is reversible as the weakly absorbed molecules can desorb by gentle annealing. While the there is an enormous body of literature on functionalization of graphene with molecules (see [22–26] for reviews), here we only concentrate on well-defined systems with molecules forming large-scale, periodic lattices on graphene.

Measuring doping level of graphene with tunneling spectroscopy is non-trivial in particular for graphene buried under a molecular adlayer with conflicting results in the literature for e.g., PTCDA adsorption [97, 199]. Assessing the effect of molecular layers on the band structure of the underlying 2D material is perhaps better carried out using PES, in particular angle-resolved photoelectron spectroscopy (ARPES). Synchrotron based high-resolution PES shows that the work function of G/SiC shifts up by $\sim 0.25$ eV upon deposition of 1 ML of PCTDA, indicating very weak hole transfer from the molecule [96, 200]. The fact that the graphene band structure remains unaltered after deposition of PTCDA or pentacene [201] has been utilized in using them as seeding layer for atomic layer deposition of thin dielectric layer (aluminum oxide) [99] or as a protecting layer for the graphene.

C$_{60}$ acts as a weak electron acceptor (EA $\approx 3.7$ eV). High resolution PES data [202] on G/SiC show a $\sim 0.15$eV upshift of the work function of the system compared to clean epitaxial graphene; this indicates very weak p-doping of graphene. Raman spectroscopy and terahertz conductivity measurement on graphene on SiO$_2$ confirm a weak p-doping effect due to C$_{60}$ deposition (estimated as $\sim 0.04$e transferred to each molecule) [203]. Additionally, the carrier mobility increases by $\sim 1500$ cm$^2$/Vs —the authors hypothesize that it is due to screening of long-range scatterers (charged impurities at G/SiO$_2$ interface) by the molecules. Two other organic molecules—octadeclphosphonic acid (OPA) (figure 10(c)) [196] and TMA (figure 10(e)) [106] assemble into well-ordered structures and cause p-doping of graphene as shown by transport and Raman measurements, respectively.

We now turn our attention to organic molecules which are strong electron acceptors e.g., TCNQ, $F_2$TCNQ, and tetracyanoethylene (TCNE). Doping of graphene due to interfacial charge transfer by these molecules has been topic of many theoretical studies [204, 205]. Sun et al [195] performed DFT calculations showing that $F_2$TCNQ, which has a higher EA than TCNQ [206], is expected to accept more charge ($0.4$e) than TCNQ ($0.33$e) (figure 10(b)). This prediction is confirmed by the ARPES experiments by Coletti et al on G/SiC [197]. G/SiC is intrinsically n-doped with the Dirac point 0.42 eV below the $E_F$ (figure 10(d)-(i)). Deposition of $F_2$TCNQ drives the Dirac point towards $E_F$; it saturates at $E_F$ after deposition molecular layer with a nominal thickness of 0.8 nm (figure 10(d)-(ii)). This indicates a
neutralization of the graphene surface due to p-type doping from the molecule. For TCNQ however, the Dirac point saturates at 0.25 eV below $E_F$ (figure 10(d)-(iii)). Thus, the p-type doping from TCNQ is weaker than its fluorinated counterpart. XPS data of $F_4$TCNQ on G/SiC further reveals that the charge transfer takes place exclusively through one pair of the terminal cyano groups with the molecules adsorbing in an upright configuration at high coverage. Another synchrotron-based PES study indicates that the work function of G/SiC (4 eV) increases with increasing surface coverage of $F_4$TCNQ, saturating at 5.3 eV after deposition of a monolayer [202]. This is associated with a 0.5 eV shift of the graphene related C1s peak to lower binding energy. The authors concluded that this is due to charge accumulation at the G/SiC interface due to strong hole doping by the molecule.

Theoretical studies of the electron donating tetra-thiophene(m) male (TTF) molecule on graphene predicted that it donates 0.1 eV to graphene, making the latter n-doped [195, 205]. UV based XPS data of chemically exfoliated graphene dispersed with TTF indicates the presence of both uncharged and positively charged sulphur [207]. This indicates electron donation to graphene by TTF.

Vanadyl phthalocyanine (VOPc), a member of the phthalocyanine family which assembles into close-packed geometry on graphene, is seen to dope it with electrons [208]. Kelvin probe microscopy on exfoliated graphene on SiO$_2$ reveals that deposition of VOPc results in an increase of the contact potential difference, indicating transfer of electrons from the molecules to graphene. Mono- and bilayer graphene (BLG) are more strongly electron-doped by the molecules compared to thicker graphene layers. $I$-$V$ measurements on graphene FETs show a downshift of the $V_{\text{CNP}}$ by $\sim 9$ V, without any degradation of carrier mobility, confirming the n-doping. Based on the experimental data, the authors concluded that each molecule donates about 0.04 e to graphene. n-doping of graphene has also been found with several different functional groups, Yokota et al [212] concluded that the doping effect can be related to the induced dipole moment in the SAM. For certain functional groups (NH$_2$C$_2$H$_4$- and C$_6$-SAM), the dipole points towards the graphene while for others (NH$_2$C$_3$H$_7$- and the fluorinated F$_{13}$-SAM), the direction of the dipole is opposite. It was found that the SAMs of first kind n-dope graphene, bringing the carrier-density to near pristine levels while the latter p-dope graphene. In another study of $I$-$V$ characteristics of CVD-graphene on SiO$_2$ passivated with different SAMs, the authors [213] concluded that for some SAMs (strongly p-doping CF$_3$-SAM and slightly n-doping CH$_3$-SAM), the doping is due to the dipole moment. But for SAMs with strong electron donating (strongly n-doping NH$_2$-SAM) or accepting groups (weakly p-doping H$_2$N$^+$-SAM), the doping is due to interfacial charge transfer.

While opening a band-gap in monolayer graphene by self-assembled molecular layers has not yet been demonstrated, this has been achieved in the case of BLG. Band gap in BLG can be opened by breaking the equivalence of the individual layers by application of an external electric field perpendicular to the layers [11], which has been shown by external electrostatic gates [215]. However, this approach requires application of complex lithographic processes and high electric fields. An alternative way to achieve this would be to generate an interlayer charge asymmetry by individually tuning the polarity and concentration of charge carriers in the top and bottom graphene layers through chemical doping. Doping by $F_4$TCNQ has been seen to open a band-gap in epitaxial BLG on SiC [197] (figure 11(c)). BLG/SiC is intrinsically n-doped with a band-gap caused by electric dipoles at G/SiC interface which break the interlayer symmetry. This manifests in ARPES data as a gap of about 0.116 eV; the Dirac point lies mid-gap, about $-0.3$ eV below the $E_F$. Increasing $F_4$TCNQ coverage drives the Dirac point close to $E_F$ (i.e., a reduction in n-doping) with an increase in the band-gap. Finally at about 2 ML coverage, the effects saturates giving a final band-gap of 0.275 eV. The authors proposed that an additional dipole at the molecule-graphene interface increases the electrostatic asymmetry, resulting in an increase of the band-gap. Deposition of $F_4$TCNQ is also seen to open a band-gap in exfoliated BLG [214] (figure 11(d)) on NH$_2$-SAM functionalized SiO$_2$ substrate. As seen form $I$-$V$ measurements, SAM functionalization leads to n-doping of graphene to almost free-standing values. Finally, $I$-$V$ measurements on graphene FETs show devices with SAMs have $V_{\text{CNP}}$ close to zero back-gate voltage and an increased electron mobility with a higher packing density of the SAM leading to better device performance (figure 11(a)).

SAMs offer the possibility to tune the reactivity of the surface by different functional groups. For example, SAMs with electron donating NH$_2$- groups n-dope graphene [211]. This was demonstrated by Raman and UPS measurements, where CVD-graphene transferred onto NH$_2$-SAM modified surface was n-doped compared to untreated or CH$_3$-SAM modified surface. $I$-$V$ data in figure 11(b), shows that NH$_2$-SAM causes reduction of $V_{\text{CNP}}$ to large negative voltages, confirming the n-doping effect. Based on a study of SAMs with several different functional groups, Yokota et al [212] concluded that the doping effect can be related to the induced dipole moment in the SAM. For certain functional groups (NH$_2$C$_2$H$_4$- and C$_6$-SAM), the dipole points towards the graphene while for others (NH$_2$C$_3$H$_7$- and the fluorinated F$_{13}$-SAM), the direction of the dipole is opposite.
the graphene and compared to an unpassivated surface, the resistance at $V_{\text{CNP}}$ is higher. Deposition of F4TCNQ is seen to drive $V_{\text{CNP}}$ to larger positive values with an accompanying increase of resistance at $V_{\text{CNP}}$. Based on a model calculation, the authors estimated the largest achieved gap as 0.124 eV. Accompanying infrared absorption data gave an estimate of the maximum optical band-gap of 0.210 eV. In both cases, the gap increased with increasing F4TCNQ surface coverage. The authors concluded that that NH2-SAM gives stable n-doping to the bottom graphene layer and F4TCNQ deposition leads to p-type doping of the top layer: the increased asymmetry results in a concomitant increase in the gap.

6. Summary and outlook

Molecular self-assembly has been typically studied on metal surfaces or on graphite, where the focus has been on understanding the fundamentals and to investigate in detail the structure of the assemblies. In the case of bulk substrates, molecular self-assembly cannot be used for a profound modification of the substrate electronic structure beyond doping or quenching surface states. Alternatively, molecular layers can be used as templates for patterning the deposition of subsequent layers.

2D materials consist of only surface atoms, and hence, adsorption of a molecular layer can completely change their electronic response. This is a strong motivation to study molecular self-assembly on 2D materials. Understanding the formation of molecular assemblies, which can differ strongly from the corresponding systems on a metal substrate, is progressing especially in the case of epitaxial graphene and hBN substrates. Close-packed molecular assemblies without intermolecular bonds or hydrogen-bonded networks are relatively well-understood. More strongly linked assemblies, in particular covalently bonded systems are still a virtual terra incognita and we lack even basic understanding of chemical reactions where the substrate is involved.

Compared to the close-packed metal surfaces, 2D materials present an inert surface on which the electronic properties arising from the self-assembled molecules are preserved. Beyond its obvious importance in fundamental research on
the electronic properties of molecular materials, this presents an unique opportunity to test monolayer thick, all-organic electronic devices. These could also be incorporated into vdW heterostructures (i.e., stacked layers of 2D materials), for additional stability and functionality. The immense flexibility in choosing the constituents of such hybrid materials makes a strong case for further studies in this field.

Molecular adlayers can help enable novel applications that are only made possible through the unique properties of 2D materials. For example, molecular layers can enable strong and precise doping profiles, which are important in formation of sharp p–n junctions. Further-reaching potential applications include profound modifications of the band structure of 2D materials by, e.g., imposing a periodic potential modulation through molecular self-assembly to generating totally novel materials where the properties of the 2D substrate and the molecular layer strongly hybridize. Beyond the application of functionalized 2D materials in the fields of catalysis, sensors, and flexible and transparent electronic materials, the combination of molecular adlayers and 2D materials in hybrid heterojunctions can open a hitherto unknown vista of materials with exciting electronic properties.

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