

Interfacial Properties and Design of Functional Energy Materials

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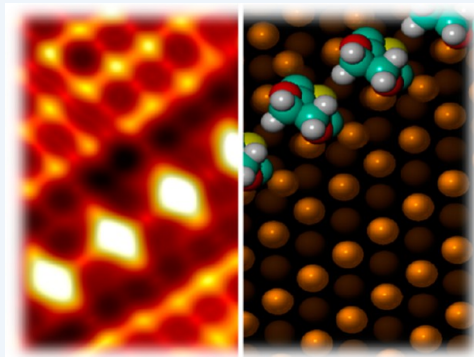
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CONSPECTUS: The vital importance of energy to society continues to demand a relentless pursuit of energy responsive materials that can bridge fundamental chemical structures at the molecular level and achieve improved functionality and performance. This demand can potentially be realized by harnessing the power of self-assembly, a spontaneous process where molecules or much larger entities form ordered aggregates as a consequence of predominately noncovalent (weak) interactions. Self-assembly is the key to bottom-up design of molecular devices, because the nearly atomic-level control is very difficult to realize in a top-down, for example, lithographic, approach. However, while function in simple systems such as single crystals can often be evaluated *a priori*, predicting the function of the great variety of self-assembled molecular architectures is complicated by the lack of understanding and control over nanoscale interactions, mesoscale architectures, and macroscale order. To establish a foundation toward delivering practical solutions, it is critical to develop an understanding of the chemical and physical mechanisms responsible for the self-assembly of molecular and hybrid materials on various support substrates.

Typical molecular self-assembly involves noncovalent intermolecular and substrate–molecule interactions. These interactions remain poorly understood, due to the combination of many-body interactions compounded by local or collective influences from the substrate atomic lattice and electronic structure. Progress toward unraveling the underlying physicochemical processes that control the structure and macroscopic physical, chemical, mechanical, electrical, and transport properties of materials increasingly requires tight integration of theory, modeling, and simulation with precision synthesis, advanced experimental characterization, and device measurements. Theory, modeling, and simulation can accelerate the process of materials understanding and design by providing atomic level understanding of the underlying physicochemical phenomena (illuminating connections between experiments). It can also provide the ability to explore new materials and conditions before they are realized in the laboratory. With tight integration and feedback with experiment, it becomes feasible to identify promising materials or processes for targeted energy applications.

In this Account, we highlight recent advances and success in using an integrated approach based on electronic structure simulations and scanning probe microscopy techniques to study and design functional materials formed from the self-assembly of molecules into supramolecular or polymeric architectures on substrates.



■ INTRODUCTION

Nanostructured materials with improved physicochemical or mechanical properties continue to be discovered. These materials offer exciting potential for technological advances that could have a positive impact on numerous sectors of the economy.¹ However, progress toward realization of this potential has been extremely challenging. A number of complications arise in regard to controlled design of the desired nanostructures and in the translation of the properties originating at the nanoscale to the mesoscale and macroscales. Additionally, while it is often possible to derive the properties of many bulk materials from the knowledge of the properties of their constituting atomic units or complexes, the properties of nanoscale systems do not necessarily manifest in the behavior of single atomic or molecular units. Rather, new properties can emerge when the materials' building blocks are arranged into nanostructures. Because these properties often arise due to

quantum phenomena and statistical fluctuations, they cannot be simply predicted by scaling with size. Therefore, theory and simulations must account for the entire nanostructure in order to provide accurate insight and predictions.

Currently, there are two broad approaches used for the design of nanoscale systems: top-down and bottom-up. The top-down routes have proven to be challenging because they often yield structures with difficult-to-predict local properties. The bottom-up approaches also pose numerous difficulties rooted in the controlled self-assembly and rapid evaluation of structure/property relationships.² This lack of control continues to limit the ability to manipulate the properties of

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nanoscale components to deliver desired collective properties. For this reason, developing a fundamental understanding of the interactions (electronic, atomic, and molecular) and dynamics of molecular building blocks is critical to enabling improved experimental control of nanoscale assemblies.^{3,4}

The capacity of achieving atomic-level engineering has been strongly enhanced by recent developments in experimental methods capable of preparing low-dimensional molecular nanosystems. In particular, methods that enable direct material preparation on a surface in ultra-high vacuum (UHV) conditions and through covalent coupling of smaller reactive precursors are useful.^{5–7} Major advantages are provided by covalent bonding such as mechanical rigidity of the structures, high thermal stability, or effective charge transport through chemical bonds. In addition, the resulting structures can be atomically characterized using standard surface science imaging techniques such as scanning tunneling microscopy (STM) and noncontact atomic force microscopy (nc-AFM)⁸ complemented with density functional theory (DFT)⁹ calculations.

This Account highlights integrated experimental and computational studies of functional materials for energy science and technology. In many cases, the results provide resolution of some of the underlying issues that prohibit the effective utilization of bottom-up self-assembly. We show examples that have effectively addressed questions such as: How do intermolecular interactions and complex correlations of atoms and molecules dictate the formation and properties of oriented nanostructures? What are the effects of reduced dimensionality? Do physical properties vary when materials are confined at surfaces/interfaces? How can these variations be harnessed to design novel functional materials?

To address these questions, we present an overview of recent progress toward understanding and ultimately providing a means for successfully manipulating, controlling, or exploiting self-assembly of materials to deliver improved energy transport, conversion, and storage properties. In particular, we show how an integrated multidisciplinary approach can successfully be used to understand how chemical and physical information encoded at the nanoscale can be used to manipulate structure and function.

■ SUBSTRATE-MEDIATED MOLECULAR SELF-ASSEMBLY

Heimel et al. provided a microscopic picture for the interface energetics of self-assembled monolayers on metals.¹⁰ This work highlighted the relevance for application to organic electronic devices. Indeed, notable experimental success has been achieved using alkanethiol chemistry,^{11,12} which leads to predictable covalent attachment of an alkane chain to a surface through a sulfur bond.^{13–15} However, the typical self-assembly of the alkane chains is thermally driven. This often leads to many defects and packing problems. In this regard, recent studies have tried to mediate some of the drawbacks by focusing on alternative molecular building blocks and different self-assembly scenarios, including the exploitation of weak noncovalent interactions between organic molecules on surfaces.¹⁶

Weak directional molecular interactions are central to self-assembly in general and are particularly important for the formation of supramolecular structures on surfaces because they provide a balance between intermolecular and molecule–surface interactions, as well as the feasibility of coordination shell saturation. Of the candidate attractive interactions,

hydrogen bonding is typically the most significant, because despite being weak, it maintains well-defined directionality, in contrast to van der Waals and ionic interactions. One recent study highlighted how a self-assembly process is governed by unique cooperative, multicenter CH/ π interactions, which offer another attractive mode for tunability via chemical functionalization.¹⁶ In this case, at low-temperature deposition of ~ 0.1 ML of phenylacetylene on Au(111), the molecules assemble into largely disordered clusters on the Au(111) surface. Annealing at ~ 120 K leads to most of the molecules on the surface rearranging into a single type of cluster with regular triangular shape and exactly six constituent phenylacetylenes (see Figure 1).

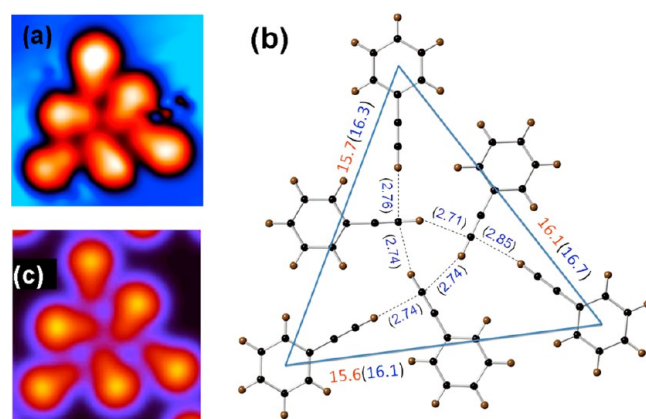


Figure 1. A high-resolution STM image of a phenylacetylene (PA) hexamer and its calculated structure. (a) Experimental STM image. (b) Computed structural model for a 2D-optimized PA hexamer. Experimental distances are given in red and calculated ones are listed between parentheses. (c) Theoretical STM image for the fully relaxed hexamer on Au(111). Adapted with permission from ref 16. Copyright 2012 American Chemical Society.

Turning to high surface coverage of phenylacetylene on Au(111), STM imaging yields a fuzzy image with a herringbone reconstruction (Figure 2b).¹⁷ The fuzziness of the image

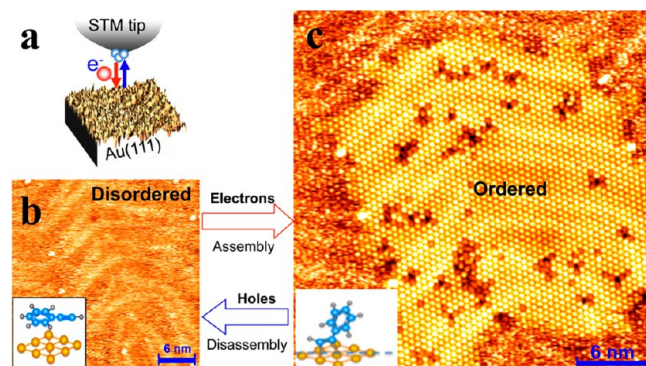


Figure 2. Transition between a disordered phase and an ordered phase by the tip-induced reaction of phenylacetylene (PA) on an Au(111) surface. (a) Schematic drawing of the experimental setup. (b) STM image of the disordered phase, with the inset showing the molecular orientation of a physisorbed PA determined from DFT calculations. (c) STM image of an ordered structure at the same location as image b after the reaction (inset shows new configuration of the PA). Adapted with permission from ref 17. Copyright 2012 American Chemical Society.

indicates a mobile molecular overlayer composed of physisorbed flat-lying phenylacetylene molecules. This image is dramatically transformed if the surface area is scanned by an STM tip with positive sample bias. Figure 2c shows that a clear ordered structure emerges, with an approximately hexagonal packing of molecular features. The ordered island slowly “grows” during scanning. Once established, the ordered structure remains stable for a long period of time, independent of tunneling conditions or even the presence of an STM tip. The area of the surface that undergoes this disorder–order transition can be hundreds of square nanometers, accommodating thousands of ordered molecules.

While the injection of hot electrons from the STM tip causes the molecules to react and self-assemble (Figure 2c), hot holes (supplied by negative sample bias) cause a highly controllable disassembly (Figure 2b). In this case, the STM tip does not have to raster the image. Instead, hot holes are injected into the surface from a single position under the tip and disassembly occurs in a large area surrounding the tip–surface junction. The order–disorder transition is reversible in the same area of the surface, allowing creation, erasure, and recreation of the ordered structures simply by variation of the tunneling conditions and scan parameters.

Clearly, the direct control over the anchor bond chemistry achieved through electronic excitation has enabled self-assembly of the molecules that do not, or even cannot, self-assemble by thermal activation. The resulting attachment of the molecules to the surface through the alkyne group is a previously unachievable result. Overall, this electron-induced excitation approach is promising for achieving “on-demand”, fast and reversible nanoscale control over the chemistry of the anchor bonds thereby enabling a new and highly controlled approach to molecular self-assembly on a surface. Local and large-scale control over the self-assembly without thermal excitation could help pave the way to new chemical design rules for self-assembly of small and large molecules in a desired pattern for electronic, photonic, and energy applications.

Nonmetal substrates have also been used to guide molecular self-assembly. Atomically thin sp^2 -bonded layers such as graphene or boron nitride (BN) grown on metal supports have attracted considerable interest due to their potential geometric corrugation that can guide the positioning of atoms, metallic clusters, or molecules. For example, graphene when used as a substrate can effectively alter the properties of molecules on its surface. A demonstration is seen by comparing copper phthalocyanine (CuPc) deposited on silicon substrates and on graphene films.¹⁸ Here the planar square-shaped CuPc molecules form edge-on layers on silicon while on a graphene substrate, they assume a face-on orientation (Figure 3). This is a particularly useful achievement because the carrier mobility is enhanced in the direction of CuPc growth that becomes perpendicular to the graphene surface due to π – π interactions.

BN/Cu(111) or BN/Ir(111) are geometrically smooth, electronically corrugated sp^2 /metal interfaces that provide another unique nanoscale template.^{19,20} The ultrathin BN spacer layer introduces new prospects compared with conventional adsorption on metal supports. For example, a reduced electronic coupling of a free-base porphine, 2H–P, to metallic states was shown by the opening of an electronic gap.¹⁹ This work enabled the visualization of the tautomerization-induced LUMO-switching and the electronic level alignment. At elevated porphine coverage, extended porous chiral Kagomé networks were formed, potentially allowing the ability to steer

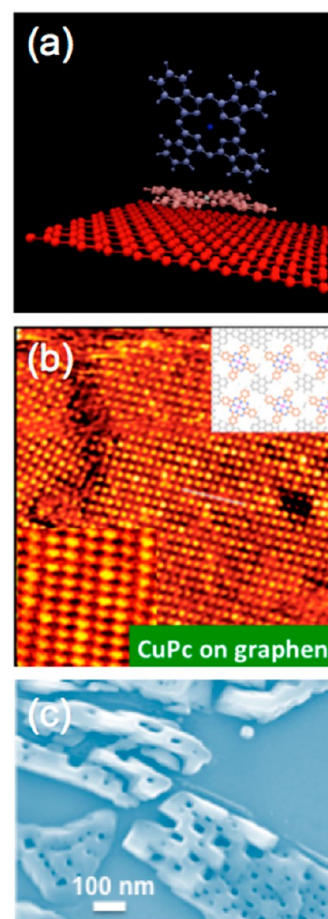


Figure 3. (a) Theoretical modeling of interactions of CuPc molecules with graphene in both face-on and side-on orientations. (b) STM image revealing that CuPc molecules align in the face-on orientation on graphene (as in the inset, right). (left inset) Higher magnification STM image. (c) SEM image of large 2D strip-like crystals of CuPc that are epitaxially aligned with the graphene surface and oriented along the graphene grain boundaries. Adapted with permission from ref 18. Copyright 2013 American Chemical Society.

the level alignment and to tune the electronic gap of surface anchored functional molecules.

Epitaxial growth of organic charge-transfer ionic salts (CTISs) composed of molecular cations and anions leads to another class of materials that may allow the synthesis of thin films of molecular conductors with strong electron correlations and electron–phonon interactions. These materials can have highly distinct properties compared with thin organic semiconductors and traditional self-assembled monolayers. CTISs exhibit a fascinating diversity of electronic ground states including metallic, charge-ordered, Mott-insulating, superconducting, and spin-liquid phases.^{21–23} A striking example of epitaxial growth and novel properties has been shown for $(\text{BETS})_2\text{GaCl}_4$ [BETS = bis(ethylenedithio)-tetraselenafulvalene] on Ag(111).²⁴ Here the occurrence of superconductivity with a T_c of 8 K implies conductivity within the molecular layer above T_c . The diversity of surface-supported multicomponent molecular structures derived from charge-transfer salts and the perseverance of cation and anion molecules provide rich opportunity for achieving correlated electron properties in ultrathin molecular films.

β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃ on Ag is another example of a CTIS (Figure 4).²⁵ Study of this system was motivated by

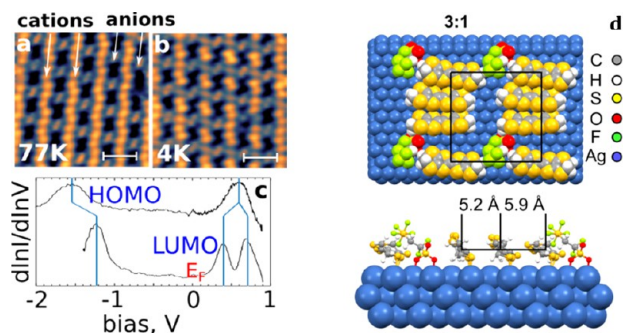


Figure 4. STM image of ET₂(SF₅CH₂CHFSO₃) on Ag(111) at 77 K (a) and 4 K (b), acquired at 350 mV. (c) STS of 1:1 (top) and 3:1 (bottom) phases revealing a net insulating property. (d) Top-view and side-view models of the 3:1 phase obtained by DFT calculations (the unit cell is outlined by black line). Adapted with permission from ref 25. Copyright 2013 American Chemical Society.

the proximity of the superconducting state to a charge-ordered insulating phase, owing to a 3/4 filled electron band. In this case, superconductivity could potentially be mediated by charge-order fluctuations rather than a more common hypothesis of antiferromagnetic spin-order fluctuations found in 1/2 filled dimerized charge-transfer salts. DFT calculations of adsorbed molecules provided evidence that they actually remain ionic, with adsorption and intermolecular binding energies comparable to that of bulk cohesive energies, thereby describing the interfacial self-assembly.

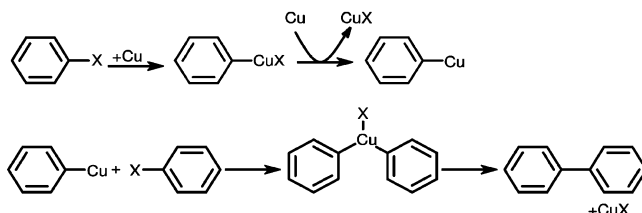
Overall there has been steady progress in the research area of surface mediated self-assembly processes. Here, it is the interplay between molecular interactions and surface electrons that is used to control the final architecture and subsequent properties of the two-dimensional patterns or assemblies. The results obtained have provided examples of the utility of this approach for controlling molecular order at an interface. This is fundamentally important to improving efficiencies of molecular and optoelectronics¹⁰ as well as for developing improved buffer layers in photovoltaic devices (for energy level alignment at electrodes).

■ COVALENT MOLECULAR NETWORKS THROUGH INTERFACIAL CHEMISTRY

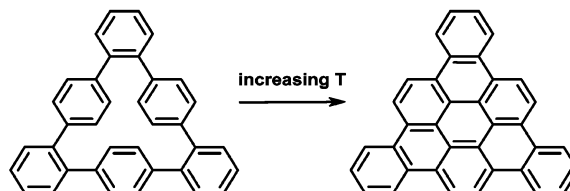
One of the great challenges in surface chemistry is to assemble aromatic building blocks into ordered structures that are mechanically robust and electronically interlinked. Here, we review examples of recent advances in this very active field.^{26,27}

Due to the well-understood carbon chemistry and the possibility of building complex hierarchical nanostructures, nanoassembly involving the creation of carbon–carbon bonds is one of the most studied on-surface reactions. Mechanisms for supramolecular reactions have been developed using a combination of elementary chemical reaction concepts such as the Ullmann coupling, cyclodehydrogenation, or radical/carbene assembly (Figure 5). In addition, these elementary processes enable the combination of carbon precursors and heteroelements, such as nitrogen, boron, or iron atoms that suggest the possibility of controlled reactions resulting in functional systems with controlled band gap alignment.²⁸

Ullmann coupling



cyclodehydrogenation



Bergman cyclization

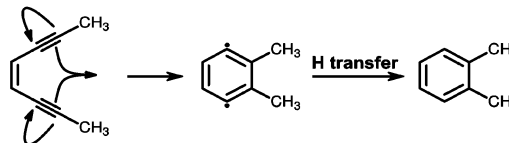


Figure 5. Mechanisms of carbon–carbon bond forming reactions: Ullmann coupling reaction of a halogeno-benzene using copper (top panel), cyclodehydrogenation of CHP to tribenzo[*a,g,m*]coronene (central panel), and Bergman cyclization of (*Z*)-octa-4-en-2,6-diyne gives *o*-xylene (bottom panel).

Ullmann coupling is an organic reaction based on catalyzed dehalogenation (commonly Br, I, and Cl halogen atoms) that was identified more than 100 years ago.²⁹ It consists of the reaction of two molecules of aryl halides with 1 equivalent of a transition metal (such as Cu) at high temperature (above 200 °C) to form biaryls and transition metal halides. Although some details on the mechanism of the Ullmann reaction are not fully understood,^{30,31} it has already been successfully used to generate C–C bonding between aromatic nuclei. The individual steps of the Ullmann reaction have been driven and monitored using a STM tip on Cu(111) facet³² for the synthesis of biphenyls from iodobenzene molecules in three reaction steps. First, tunneling electrons from the STM tip were used to induce the dissociation of iodobenzene to iodine and a phenyl product. Second, the STM tip was employed to separate iodine atoms and phenyl molecules by lateral manipulation. Finally, a phenyl molecule on one side of the Cu substrate is moved by the STM tip to be close to another phenyl to prepare for their association via a voltage pulse.

Grill et al. reported a successful methodology to assemble 0D, 1D, and 2D tetraphenylporphyrin (TPP) assemblies on Au(111)³³ where TPP monomers were used with different numbers and positions of bromine atoms (Figure 6). Two reaction steps were accomplished to create these nanostructures: the first was the deposition of the monomer molecule on Au(111) at room temperature along with annealing to cleave the carbon–halogen bond; the second was achieved by heating the porphyrin monomer to free the bromine atoms, thereby depositing the dehalogenated intermediates directly on the surface with no subsequent annealing.

Lipton-Duffin et al. also exploited the Ullmann coupling scheme to synthesize two different polyphenylene structures:

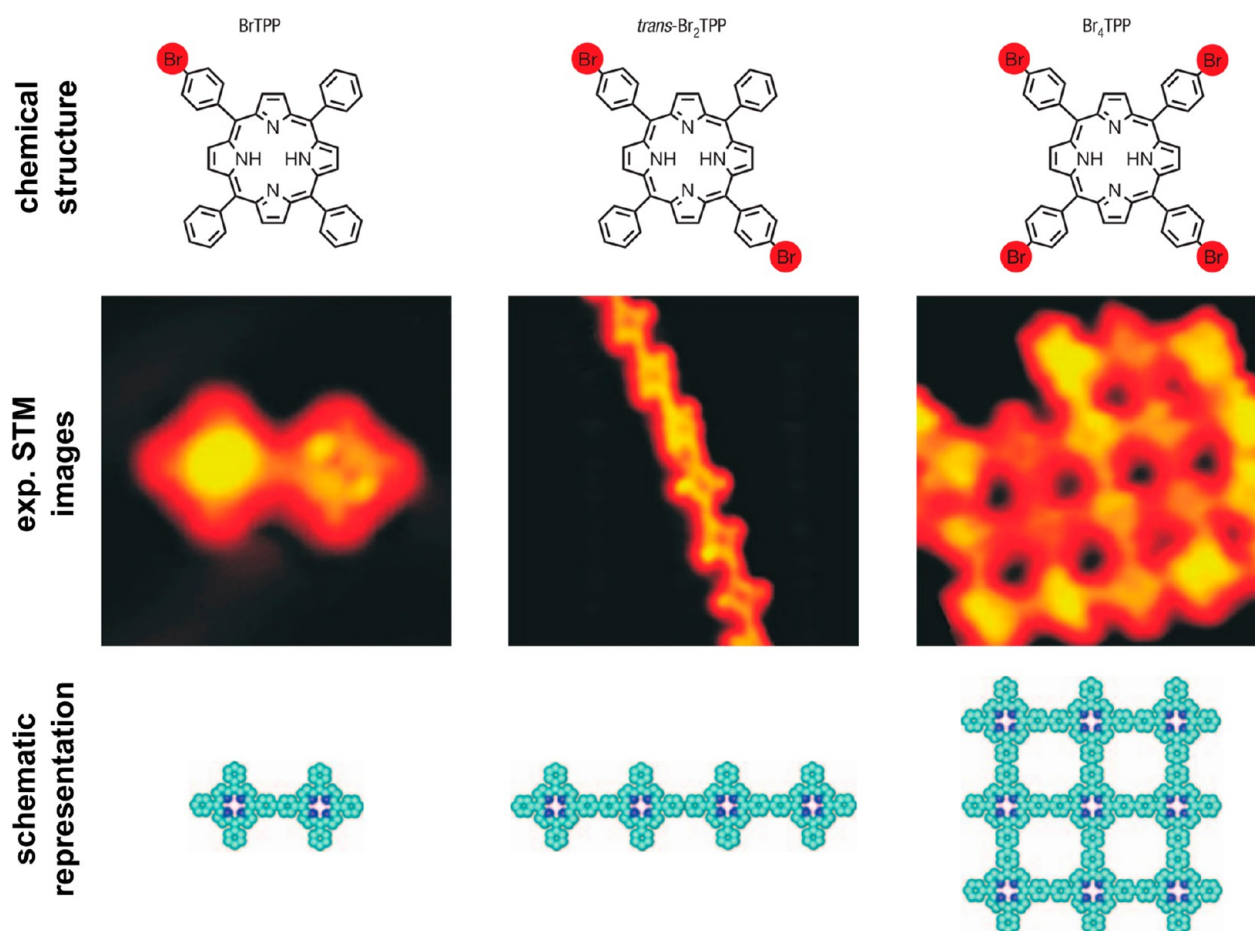


Figure 6. Zero-, one-, and two-dimensional self-assembly of polyporphyrins obtained through Ullmann coupling reactions on Au(111) surface. Reproduced with permission from ref 33. Copyright 2007 Nature Publishing Group.

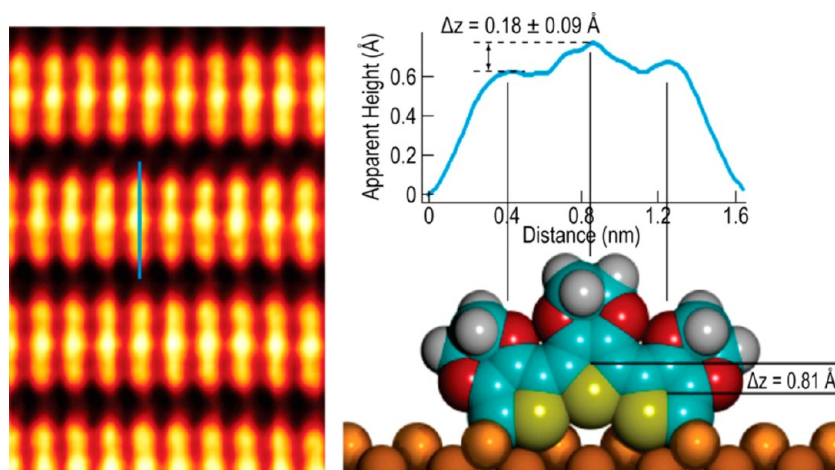


Figure 7. Formation of epitaxially confined *cis*-PEDOT on a Cu(110) surface and comparison of the calculated trimer geometry with STM-measured structures. Adapted with permission from ref 38. Copyright 2009 National Academy of Sciences.

meta (PMP) and para-polyphenylene (PPP) on Cu(110) surface under UHV conditions by dehalogenation from 1,4 diiodobenzene (para-dIB) and 1,3-diiodobenzene (meta-dIB) precursors.³⁴ The PPP chains constitute the final product of polymerizing para-dIB monomers by annealing at 500 K, leading to discrete aligned polymer chains adsorbed on the Cu(110) surface and separated by iodine adatoms. Furthermore, the polymerization of meta-dIB on Cu(110) produced

two different structures: zigzag lines and macrocycles. These results illustrate that the geometry of the final polymerized structure is dependent on the position of the halogen substituent on the molecule. While this methodology relies predominantly on the chemical nature of the monomers to create differently shaped networks, the effect of metal substrates is clearly critical. In that respect, Bieri et al. demonstrated the importance of substrate reactivity by performing a series of

experiments using the same precursor (cyclohexa-*m*-phenylene, CHP) on three different metal substrates: Ag(111), Au(111), and Cu(111).³⁵ The combination of experiments and simulations indicates that Cu(111) presents the most reactive sites and a reduced mobility of the adsorbed molecules. Björk et al. demonstrated using DFT calculations that energy barriers for the dehalogenation, recombination, and diffusion processes are dependent on both the metal substrate and the nature of the halogen atoms used for the Ullmann coupling.³⁰

Di Giovannantonio et al. recently used a combination of STM, X-ray photoelectron spectroscopy, and low energy electron diffraction to develop insight into surface-catalyzed dehalogenative polymerization by analyzing the organometallic intermediate and its evolution into planar polymeric structures.³⁶ The structural conformation of substrate-bound phenylene intermediates generated from 1,4-dibromobenzene precursors on Cu(110) provided considerable insight into the key stabilizing role of the halogen atoms. Other recent studies of bromobenzene on Cu have illustrated how biphenyl forms on the surface via a highly mobile organometallic intermediate in which two phenyl groups extract and bind a single surface Cu atom.³⁷

The formation of epitaxially ordered arrays of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) was also successfully demonstrated using a similar technique³⁸ for a surface-confined growth of ordered arrays of electrically conducting polymer chains on metal. This technique constitutes a potential method for growing molecular wires for light harvesting and optoelectronic applications. The results revealed growth of PEDOT chains using the (110) facet of copper simultaneously as a template and catalyst for polymerization (Figure 7). In general, this method provides a way to assemble aromatic building blocks into ordered structures and is extendable to other halogen-terminated molecules for producing unique, epitaxially aligned, conjugated polymers.

Another example of substrate-templated and surface electron catalyzed polymerization was demonstrated for phenylacetylene on Cu(100)³⁹ where a controllable surface-coordinated linear polymerization of long poly(phenylacetylenyl) chains induces their self-organization into a “circuit-board” pattern on a Cu(100) surface (Figure 8). The polymerization is confined epitaxially to the copper lattice, despite the over 10% strain along the polymer C–C backbone. Interestingly, polymerization and depolymerization reactions could be controlled locally at the nanoscale by using a charged metal tip (Figure 8 e), thereby offering possibilities for precisely controlling conjugated chain-growth polymerization at low temperature.

Ullmann coupling can also be followed by cyclodehydrogenation to synthesize graphene materials with atomic precision. Cai et al. developed this two-step bottom-up strategy to demonstrate the fabrication of armchair graphene nanoribbons (GNRs) and chevron- or wiggly- like systems (GNWs).^{40,41} The synthesis performed using different monomers on the Au(111) and Ag(111) surfaces leads to the formation of armchair GNRs by the deposition of different types of monomers onto a surface held at monomer-dependent temperature to induce the dehalogenation process and radicals addition. Next, the systems are annealed at higher temperature to trigger the cyclodehydrogenation (Figure 9).

The manipulation of carbon–carbon bonds on metal surfaces using other carbon chemistries (such as carbon radical coupling, cyclization, or carbenes) has been developed more recently. Advances in scanning probe microscopy now provide

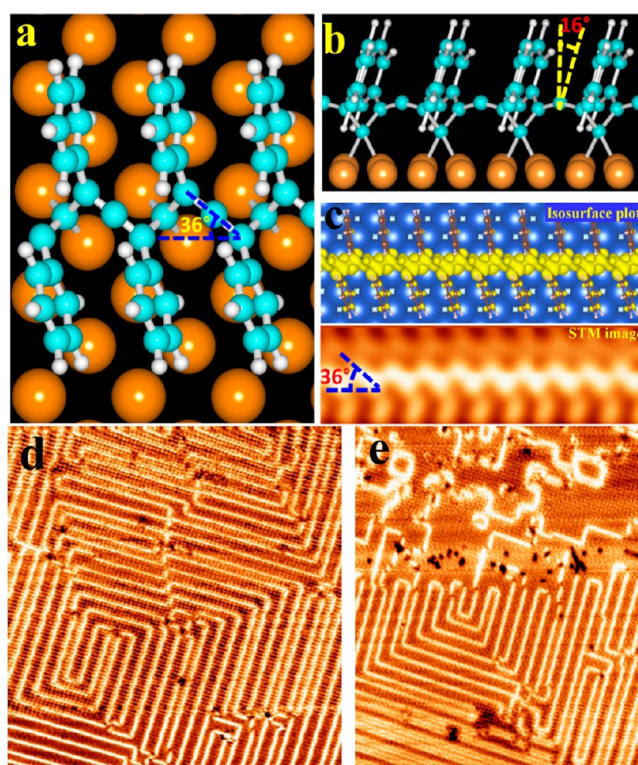


Figure 8. (a) Top and (b) Side views of the calculated relaxed conformation of periodic cis-poly(phenylacetylene)s adsorbed on Cu(100) (cyan, carbon; orange, copper; light gray, hydrogen). (c) High resolution STM image (lower panel) and the calculated isosurface plot for a section of the polymerized structure (upper panel). (d) “Circuit board” polymer pattern; stars mark points at which bias is applied. Panel e shows subsequent depolymerization. Adapted with permission from ref 39. Copyright 2013 Nature Publishing Group.

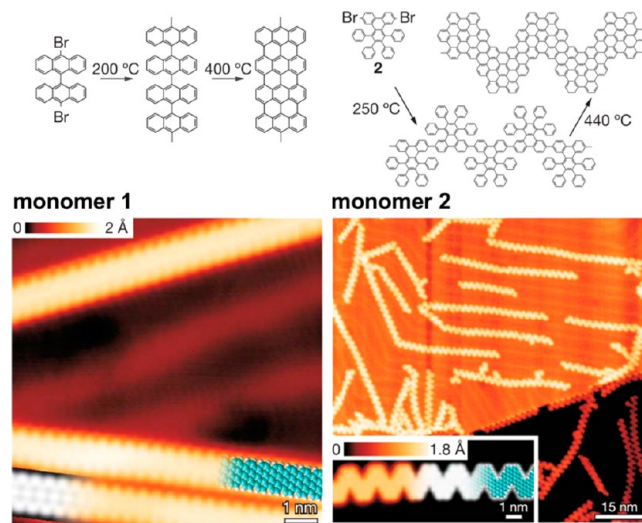


Figure 9. Ullmann coupling followed by cyclodehydrogenation reaction. Experimental STM images for two monomer precursors, 1 leading to $N = 7$ AGNRs and from precursor 2, leading to GNWs. Reproduced with permission from ref 41. Copyright 2010 Nature Publishing Group.

the necessary tools to visualize not only the frontier orbitals of chemical reaction partners and products but also the internal covalent bond configurations. For instance, de Oteyza et al.

studied the products of a thermally induced enediyne cyclization of 1,2-bis((2-ethynylphenyl)ethynyl)benzene on Ag(110) facet.⁴² Eneidyne exhibit a variety of radical cyclization processes known to compete with traditional Bergman cyclization.⁴³ To directly image these products with subnanometer spatial resolution, the cyclization reaction was thermally activated on an atomically clean metallic surface, under UHV conditions, using STM and nc-AFM to probe both the reactant and final products at the single-molecule level (Figure 10). The bond-resolved single-molecule imaging

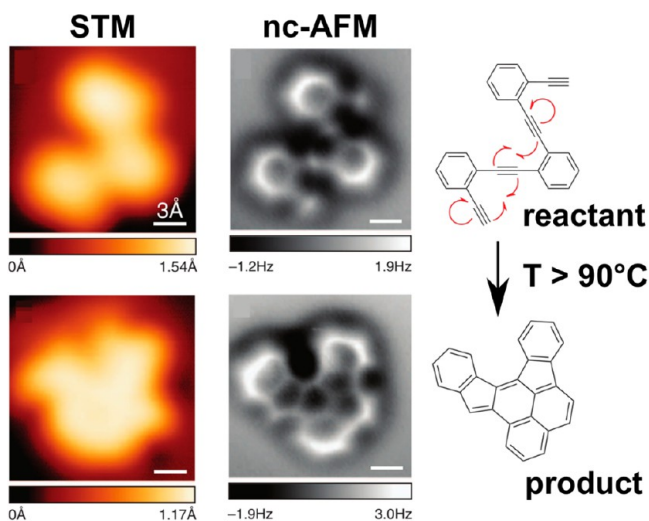


Figure 10. Comparison of STM images, nc-AFM images, and structures for molecular reactant (upper panels) and products (lower panels) from enediyne cyclization on Ag(100). Reproduced with permission from ref 42. Copyright 2013 AAAS.

allowed extraction of an exhaustive picture and unparalleled insight into the chemistry involved in complex enediyne cyclization cascades on Ag(100) surfaces.

Control over defects (conformation) in polymeric materials as well as enhanced long-range molecular order is a major achievement demonstrated in a number of the examples discussed in this section. Additionally, the assembly of aromatic building blocks into ordered polymeric structures that are mechanically robust, defect free (conformational defects), and electronically interlinked enables a significant enhancement in the electronic transport properties that will manifest into improved efficiencies in optoelectronic, chemical sensor, and photovoltaic applications, as well as mechanical properties for structural materials.

■ POLARIZATION-INDUCED MOLECULAR ORBITAL RENORMALIZATION AT MOLECULE–METAL INTERFACE

The interest in using organic molecules as components for nanoscale electronics and optoelectronics has prompted the need for a quantitative understanding of electronic processes taking place at the organic–metal interfaces.^{10,44} However, understanding and controlling molecule–metal contacts has proven challenging, especially at the single-molecule limit.⁴⁵ This highlights the difficulty of predicting intensity of electronic current flowing across a molecule on the sole basis of its gas phase properties. A number of experiments have been carried out to probe molecular systems adsorbed on metallic surfaces to highlight the significant changes in the electronic structures

of individual molecules and molecular layers on metal surfaces as a function of coverage,⁴⁶ substrate,⁸ molecule–substrate separation,⁴⁷ and conformation.⁴⁸ Many of the changes in molecular electronic structure have been attributed to polarization effects at molecule–metal interfaces. These effects, which cannot be easily captured in a mean-field approximation, are related to image charge formation for weak coupling and dynamic charge transfer for strong coupling.^{45,49–52}

The deficiencies of DFT to account for the details of molecule–metal interfaces are well-known: the Kohn–Sham energies are not designed to be good representations of molecular orbital energies due to, among other effects, self-interaction errors.⁵³ Moreover, the electrostatic polarization from the metal substrate is a many-body effect that is typically missed by DFT with the majority of existing exchange–correlation functionals.^{49,53} In contrast, by explicitly computing many-body screening effects, the quasi-particle GW approximation is able to capture the required corrections.^{45,49,53–55} The success of this correction is illustrated in Figure 11 for a

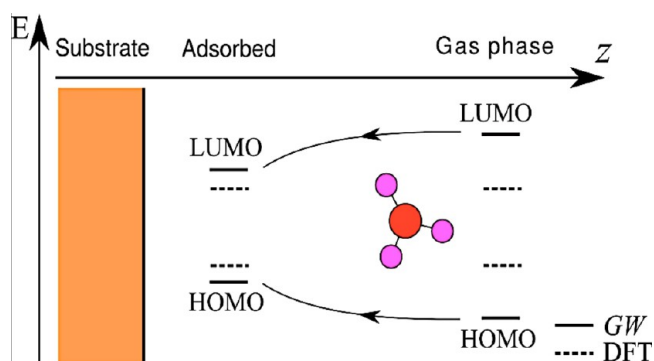


Figure 11. Relative alignment of a molecule's HOMO and LUMO energy levels as it approaches a metallic surface. In the weak coupling regime, the HOMO–LUMO gap is reduced due to substrate polarization caused by the formation of an image charge inside the substrate. In the strong coupling regime, dynamic charge transfer between molecule and metal (stronger polarization) reduces the gap further.

benzene molecule in the gas phase. Interestingly, DFT results can be consistent with GW in some cases, since self-interaction corrections increase a molecule's HOMO–LUMO gap, while substrate polarization effects reduce it upon adsorption, as shown by Garcia-Lastra et al.⁵⁴ However, the relative size of the two contributions will in general depend on the shape of the molecule, its orientation with respect to the surface, the molecule–surface distance, and the type of substrate. In other words, only under fortuitous conditions can the two effects cancel out.

Accurate descriptions of molecular levels on a substrate are critical.⁵⁰ A typical example of this effect is the conductance of molecule–metal junctions.⁵⁷ In most cases of molecular junctions, the computed conductance by DFT often substantially exceeds measured values due to inaccurate descriptions of HOMO and LUMO levels by DFT.^{55,56,58} For a single-molecule benzenediamine–gold junction, Quek et al. determined that the computed conductance obtained within the generalized gradient approximation (GGA) in DFT is close to an order of magnitude larger than that in experiment⁵⁶ (Figure 12). The orbital renormalization due to the self-energy correction and surface polarization effects shifts both the

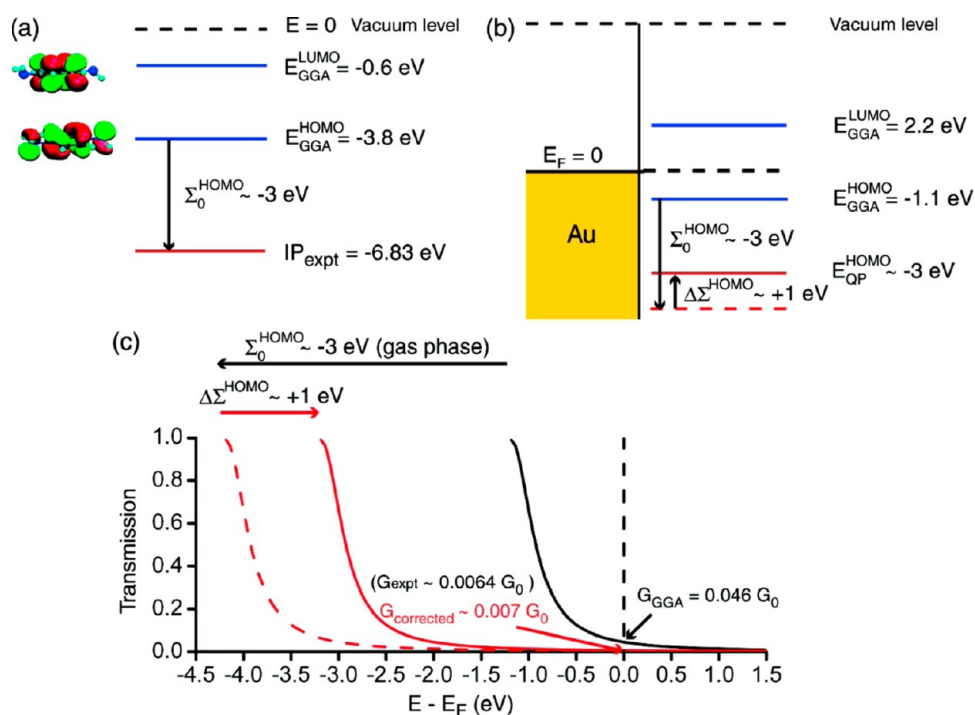


Figure 12. Example of molecular state renormalization in a benzenediamine–gold junction. The self-energy corrections are shown (a) in the gas phase and (b) in the junction. In this figure, GGA refers to the generalized gradient approximation in DFT, Σ_0^{HOMO} refers to the self-energy correction to the GGA HOMO eigenvalue, E_{GGA}^{HOMO} , in the gas phase. In the junction, polarization effects result in a further self-energy correction, $\Delta\Sigma^{HOMO}$, to E_{GGA}^{HOMO} . (c) Changes in transmission curve due to self-energy correction to the HOMO level in the junction. Black, DFT transmission; solid red, transmission curve after E_{GGA}^{HOMO} has been shifted to the estimated quasiparticle HOMO level, E_{QP}^{HOMO} , in the junction. Reproduced with permission from ref 56. Copyright 2007 American Chemical Society.

HOMO and LUMO levels away from the Fermi level, resulting in a significantly lower conductance in good agreement with experiment (solid red line in Figure 12c), further illustrating that the inclusion of both self-energy corrections and substrate polarization effects are necessary to model nanoscale transport in molecular junctions.^{59,60}

In addition to affect the orbital energies and conductance at molecule–metal interfaces, surface polarization can also lead to the renormalization of optical excitations of a molecule. Garcia-Lastra et al. showed that when a benzene molecule is placed outside a metal surface, the enhanced screening from the metal due to polarization effects reduces the exciton binding energies by several electronvolts and the optical excitation energies by up to 1 eV depending on the size of the transition-generated dipole.⁶¹ For CO molecules adsorbed on the surface of a prototypical insulator–semiconductor interface, NaCl/Ge(001), Freysoldt et al. have found that polarization effects also noticeably affect the excitation spectrum of molecules.⁶²

Surface polarization-induced orbital renormalization and gap reduction are not limited to individual molecules on a metal surface. Similar phenomena have been reported for molecular clusters⁶³ and self-assembled molecular layers (SAMs).^{41,64} For example, atomically precise one-dimensional straight and chevron-like graphene nanoribbons fabricated by self-assembly of small organic molecules on a gold substrate^{41,64} have enabled a quantitative comparison between STS and theoretical studies. This work showed that the gas-phase HOMO–LUMO gaps in such hydrocarbon nanowires⁶⁵ are reduced by as much 0.7–1.4 eV upon adsorption due to substrate polarization.^{65–67}

Currently, DFT cannot be systematically replaced by GW due to the high computational cost associated with the evaluation of a fully consistent GW approach. While GW

provides a reasonable description of the nonlocal surface polarization effects necessary to understand molecule–metal interfaces,⁴⁵ these calculations become prohibitively expensive for complex systems with more than 100 atoms.⁴⁹ However, when a molecule is weakly adsorbed on a metal surface, the polarization effects can be captured using an effective image charge model as an alternative to the full GW calculations.^{45,54,56,61,68} The image potential moves all the molecular levels by the same absolute shift but with opposite signs for occupied and unoccupied levels, leading to a narrower HOMO–LUMO gap at the interface. Despite its simplicity, the image charge model captures the essence of the physics governing the polarization-induced orbital renormalization. In many instances, a hybrid method combining GW for gas-phase molecules and the image charge model for surface polarization yields remarkably good molecular orbital renormalization consistent with full GW calculations and experimental measurements.^{45,54,56} It is also notable that DFT approaches that include exact exchange can often be effective for describing molecular energy levels and band gaps.⁶⁹ For example, it has been shown that the hybrid DFT functionals such as Heyd, Scuseria, and Ernzerhof (HSE06) can frequently describe band gaps to within the accuracies of GW.^{70–73}

In closing, we note that computational methods based on electronic structure theory (DFT, GW, wave function based) are limited to the study of modest length scales.⁷⁴ While this is often adequate for many nanoscale systems of interest, it cannot yet bridge length or time scales from molecules to an energy device (e.g., a photovoltaic cell). To more completely address how chemical and physical information encoded at the nanoscale translates structure, dynamics, and function at meso-

and macroscales will require continued advances in theory and multiscale simulation.

■ CONCLUSIONS AND PERSPECTIVES

The propensity of utilizing interfacial electronic structure as a nanoscale structural and chemical scaffold for the creation of novel materials, precise assembly, and enhanced chemistry, has been discussed. The nature of the interface and the structure/dynamics of the components dramatically impact mechanical properties and processability, ion conductivity and molecular transport, as well as viscoelastic and optical properties. Control of interfacial and nanostructure (orientation and bonding) impacts a broad range of present and future energy materials, including organic photovoltaics, energy storage, fuel cells, efficient catalytic materials, membranes for CO₂ capture, gas and water purification, and stronger lightweight materials that can result in energy savings. Additionally, the study of this area of nanoscience continues to provide advances for the design of improved materials for electronic devices and sensors as well as to address future challenges in integrating materials with exceptional properties into other application areas.

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Notes

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■ REFERENCES

- (1) Nanoscience and Technology: A Collection of Reviews from Nature Journals, 1st ed.; Rogers, P. World Scientific and Nature Publishing Group: Singapore and London, 2009.
- (2) Barth, J. V.; Costantini, G.; Kern, K. Engineering atomic and molecular nanostructures at surfaces. *Nature* **2005**, *437*, 671–679.
- (3) Han, P.; Weiss, P. S. Electronic substrate-mediated interactions. *Surf. Sci. Rep.* **2012**, *67*, 19–81.
- (4) Niu, T.; Li, A. Exploring single molecules by scanning probe microscopy: Porphyrin and phthalocyanine. *J. Phys. Chem. Lett.* **2013**, *4*, 4095–4102.
- (5) Bartels, L. Tailoring molecular layers at metal surfaces. *Nat. Chem.* **2010**, *2*, 87–95.
- (6) Champness, N. R. Surface chemistry: Building with molecules. *Nat. Nanotechnol.* **2007**, *2*, 671–672.
- (7) Perepichka, D. F.; Rosei, F. Extending polymer conjugation into the second dimension. *Science* **2009**, *323*, 216–217.
- (8) Fukagawa, H.; Yamane, H.; Kataoka, T.; Kera, S.; Nakamura, M.; Kudo, K.; Ueno, N. Origin of the highest occupied band position in pentacene films from ultraviolet photoelectron spectroscopy: Hole stabilization versus band dispersion. *Phys. Rev. B* **2006**, *73*, No. 245310.
- (9) Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Phys. Rev.* **1964**, *136*, B864–B871.
- (10) Heimel, G.; Romaner, L.; Zojer, E.; Bredas, J.-L. The interface energetics of self-assembled monolayers on metals. *Acc. Chem. Res.* **2008**, *41*, 721–729.
- (11) Fan, F. R. F.; Yang, J.; Cai, L. T.; Price, D. W.; Dirk, S. M.; Kosynkin, D. V.; Yao, Y.; Rawlett, A. M.; Tour, J. M.; Bard, A. J. Charge transport through self-assembled monolayers of compounds of interest in molecular electronics. *J. Am. Chem. Soc.* **2002**, *124*, 5550–5560.
- (12) Mantooth, B. A.; Weiss, P. S. Fabrication, assembly and characterization of molecular electronic components. *Proc. IEEE* **2003**, *91*, 1785–1802.
- (13) Fenter, P.; Eberhardt, A.; Eisenberger, P. Self-assembly of n-alkyl thiols as disulfides on Au(111). *Science* **1994**, *266*, 1216–1218.
- (14) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Self-assembled monolayers of thiolates on metals as a form of nanotechnology. *Chem. Rev.* **2005**, *105*, 1103–1169.
- (15) Wang, S.; Lu, W.; Zhao, Q.; Bernholc, J. Resonant coupling and negative differential resistance in metal/ferrocenyl alkanethiolate/STM structures. *Phys. Rev. B* **2006**, *74*, No. 195430.
- (16) Li, Q.; Han, C.; Horton, S. R.; Fuentes-Cabrera, M.; Sumpter, B. G.; Lu, W.; Bernholc, J.; Maksymovych, P.; Pan, M. Supramolecular self-assembly of π -conjugated hydrocarbons via 2D cooperative CH/ π interaction. *ACS Nano* **2012**, *6*, 566–572.
- (17) Li, Q.; Han, C.; Fuentes-Cabrera, M.; Terrones, H.; Sumpter, B. G.; Lu, W.; Bernholc, J.; Yi, J.; Gai, Z.; Baddorf, A. P.; Maksymovych, P.; Pan, M. Electronic control over attachment and self-assembly of alkyne groups on gold. *ACS Nano* **2012**, *6*, 9267–9275.

- (18) Xiao, K.; Deng, W.; Keum, J. K.; Yoon, M.; Vlassiouk, I. V.; Clark, K. W.; Li, A.-P.; Kravchenko, I. I.; Gu, G.; Payzant, A.; Sumpter, B. G.; Smith, S. C.; Browning, J. F.; Geohagan, D. B. Surface-induced orientation control of CuPc molecules for the epitaxial growth of highly ordered organic crystals on graphene. *J. Am. Chem. Soc.* **2013**, *135*, 3680–3687.
- (19) Joshi, S.; Bischoff, F.; Koitz, R.; Eciya, D.; Seufert, K.; Seitsonen, A. P.; Hutter, J.; Diller, K.; Urgel, J. I.; Sachdev, H.; Barth, J. V.; Auwarter, W. Control of molecular organization and energy level alignment by an electronically nanopatterned boron nitride TEM. *ACS Nano* **2014**, *8*, 430–442.
- (20) Schulz, F.; Drost, R.; Hämäläinen, S. K.; Liljeroth, P. Templated self-assembly and local doping of molecules on epitaxial hexagonal boron nitride. *ACS Nano* **2013**, *7*, 11121–11128.
- (21) Wosnitzer, J. Perspectives on the nature of superconductivity in organic metals. *J. Low Temp. Phys.* **1999**, *117*, 1701–1710.
- (22) Wosnitzer, J. Quasi-two-dimensional organic superconductors. *J. Low Temp. Phys.* **2007**, *146*, 641–667.
- (23) Singleton, J.; Mielke, C. Quasi-two-dimensional organic superconductors. *Contemp. Phys.* **2002**, *43*, 63–96.
- (24) Clark, K.; Hassanien, A.; Khan, S.; Braun, K.-F.; Tanaka, H.; Hla, S.-W. Superconductivity in just four pairs of (BETS)₂GaCl₄ molecules. *Nat. Nanotechnol.* **2010**, *5*, 261–265.
- (25) Rojas, G. A.; Ganesh, P.; Kelly, S. J.; Sumpter, B. G.; Schlueter, J. A.; Maksymovych, P. Ionic decomposition of charge transfer salts driven by surface epitaxy. *J. Phys. Chem. C* **2013**, *117*, 19402–19408.
- (26) El Garah, M.; MacLeod, J. M.; Rosei, F. Covalently bonded networks through surface-confined polymerization. *Surf. Sci.* **2013**, *613*, 6–14.
- (27) Franc, G.; Gourdon, A. Covalent networks through on-surface chemistry in ultra-high vacuum: State-of-the-art and recent developments. *Phys. Chem. Chem. Phys.* **2011**, *13*, 14283–14292.
- (28) Bronner, C.; Stremlau, S.; Gille, M.; Brausse, F.; Haase, A.; Hecht, S.; Tegeder, P. Aligning the band gap of graphene nanoribbons by monomer doping. *Angew. Chem. Int. Ed.* **2013**, *52*, 4422–4425.
- (29) Fanta, P. E. Ullmann synthesis of biaryls. *Synthesis* **1974**, 9–21.
- (30) Bjork, J.; Hanke, F.; Stafstrom, S. Mechanisms of halogen-based covalent self-assembly on metal surfaces. *J. Am. Chem. Soc.* **2013**, *135*, 5768–5775.
- (31) Nguyen, M.-T.; Pignedoli, C. A.; Passerone, D. An ab initio insight into the Cu(111)-mediated Ullmann reaction. *Phys. Chem. Chem. Phys.* **2011**, *13*, 154–160.
- (32) Hla, S. W.; Bartels, L.; Meyer, G.; Rieder, K. H. Inducing all steps of a chemical reaction with the scanning tunneling microscope tip: Towards single molecule engineering. *Phys. Rev. Lett.* **2000**, *85*, 2777–2780.
- (33) Grill, L.; Dyer, M.; Lafferentz, L.; Persson, M.; Peters, M. V.; Hecht, S. Nano-architectures by covalent assembly of molecular building blocks. *Nat. Nanotechnol.* **2007**, *2*, 687–691.
- (34) Lipton-Duffin, J. A.; Ivashenko, O.; Perepichka, D. F.; Rosei, F. Synthesis of polyphenylene molecular wires by surface-confined polymerization. *Small* **2009**, *5*, 592–597.
- (35) Bieri, M.; Nguyen, M.-T.; Groning, O.; Cai, J. M.; Treier, M.; Ait-Mansour, K.; Ruffieux, P.; Pignedoli, C. A.; Passerone, D.; Kastler, M.; Mullen, K.; Fasel, R. Two-dimensional polymer formation on surfaces: Insight into the roles of precursor mobility and reactivity. *J. Am. Chem. Soc.* **2010**, *132*, 16669–16676.
- (36) Di Giovannantonio, M.; El Garah, M.; Lipton-Duffin, J.; Meunier, V.; Cardenas, L.; Revurat, Y. F.; Cossaro, A.; Verdini, A.; Perepichka, D. F.; Rosei, F.; Contini, G. Insight into organometallic intermediate and its evolution to covalent bonding in surface-confined Ullmann polymerization. *ACS Nano* **2013**, *7*, 8190–8198.
- (37) Lewis, E. A.; Murphy, C. J.; Liriano, M. L.; Sykes, E. C. H. Atomic-scale insight into the formation, mobility and reaction of Ullmann coupling intermediates. *Chem. Commun.* **2014**, *50*, 1006–1008.
- (38) Lipton-Duffin, J. A.; Miwa, J. A.; Kondratenko, M.; Ciccoira, F.; Sumpter, B. G.; Meunier, V.; Perepichka, D. F.; Rosei, F. Step-by-step growth of epitaxially aligned polythiophene by surface-confined reaction. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 11200–11204.
- (39) Li, Q.; Owens, J. R.; Han, C. B.; Sumpter, B. G.; Lu, W.; Bernholc, J.; Meunier, V.; Maksymovych, P.; Fuentes-Cabrera, M.; Pan, M. Self-organized and Cu-coordinated surface linear polymerization. *Sci. Rep.* **2013**, *3*, No. 2102.
- (40) Girão, E. C.; Liang, L.; Cruz-Silva, E.; Filho, A.; Meunier, V. Emergence of atypical properties in assembled graphene nanoribbons. *Phys. Rev. Lett.* **2011**, *107*, No. 135501.
- (41) Cai, J. M.; Ruffieux, P.; Jaafar, R.; Bieri, M.; Braun, T.; Blankenburg, S.; Muoth, M.; Seitsonen, A. P.; Saleh, M.; Feng, X.; Mullen, K.; Fasel, R. Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* **2010**, *466*, 470–473.
- (42) de Otayza, D. G.; Gorman, P.; Chen, Y.-C.; Wickenburg, S.; Riss, A.; Mowbray, D. J.; Etkin, G.; Pedramrazi, Z.; Tsai, H.-Z.; Rubio, A.; Crommie, M. F.; Fischer, F. R. Direct imaging of covalent bond structure in single-molecule chemical reactions. *Science* **2013**, *340*, 1434–1437.
- (43) Jones, R. R.; Bergman, R. G. p-Benzyne. Generation as an intermediate in a thermal isomerization reaction and trapping evidence for the 1,4-benzenediyl structure. *J. Am. Chem. Soc.* **1972**, *94*, 660–661.
- (44) Nitzan, A.; Ratner, M. A. Electron transport in molecular wire junctions. *Science* **2003**, *300*, 1384–1389.
- (45) Neaton, J. B.; Hybertsen, M. S.; Louie, S. G. Renormalization of molecular electronic levels at metal-molecule interfaces. *Phys. Rev. Lett.* **2006**, *97*, No. 216405.
- (46) Yamane, H.; Yoshimura, D.; Kawabe, E.; Sumii, R.; Kanai, K.; Ouchi, Y.; Ueno, N.; Seki, K. Electronic structure at highly ordered organic/metal interfaces: Pentacene on Cu(110). *Phys. Rev. B* **2007**, *76*, No. 165436.
- (47) Repp, J.; Meyer, G.; Paavilainen, S.; Olsson, F. E.; Persson, M. Scanning tunneling spectroscopy of Cl vacancies in NaCl films: Strong electron-phonon coupling in double-barrier tunneling junctions. *Phys. Rev. Lett.* **2005**, *95*, No. 225503.
- (48) Comstock, M. J.; Levy, N.; Kirakosian, A.; Cho, J.; Lauterwasser, F.; Harvey, J. H.; Strubbe, D. A.; Frechet, J. M. J.; Trauner, D.; Louie, S. G.; Crommie, M. F. Reversible photomechanical switching of individual engineered molecules at a metallic surface. *Phys. Rev. Lett.* **2007**, *99*, No. 038301.
- (49) Sau, J. D.; Neaton, J. B.; Choi, H. J.; Louie, S. G.; Cohen, M. L. Electronic energy levels of weakly coupled nanostructures: C60-metal interfaces. *Phys. Rev. Lett.* **2008**, *101*, No. 026804.
- (50) Thygesen, K. S.; Rubio, A. Renormalization of molecular quasiparticle levels at metal-molecule interfaces: Trends across binding regimes. *Phys. Rev. Lett.* **2009**, *102*, No. 046802.
- (51) Tomba, G.; Stengel, M.; Schneider, W.-D.; Baldereschi, A.; De Vita, A. Supramolecular self-assembly driven by electrostatic repulsion: The 1D aggregation of rubrene pentagons on Au(111). *ACS Nano* **2010**, *4*, 7545–7551.
- (52) Wang, L.; Chen, S.; Liu, L.; Qi, D. C.; Gao, X.; Wee, A. T. S. Thickness-dependent energy level alignment of rubrene adsorbed on Au(111). *Appl. Phys. Lett.* **2007**, *90*, No. 132121.
- (53) Li, Y.; Lu, D. Y.; Galli, G. Calculation of quasi-particle energies of aromatic self-assembled monolayers on Au(111). *J. Chem. Theory Comput.* **2009**, *5*, 881–886.
- (54) Garcia-Lastra, J. M.; Rostgaard, C.; Rubio, A.; Thygesen, K. S. Polarization-induced renormalization of molecular levels at metallic and semiconducting surfaces. *Phys. Rev. B* **2009**, *80*, No. 245427.
- (55) Thygesen, K. S. Impact of exchange-correlation effects on the IV characteristics of a molecular junction. *Phys. Rev. Lett.* **2008**, *100*, No. 166804.
- (56) Quek, S. Y.; Venkataraman, L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B. Amine-gold linked single-molecule circuits: Experiment and theory. *Nano Lett.* **2007**, *7*, 3477–3482.
- (57) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. Conductance of a molecular junction. *Science* **1997**, *278*, 252–254.
- (58) Xiao, X. Y.; Xu, B. Q.; Tao, N. J. Measurement of single molecule conductance: Benzenedithiol and benzenedimethanethiol. *Nano Lett.* **2004**, *4*, 267–271.

(59) Delaney, P.; Greer, J. C. Correlated electron transport in molecular electronics. *Phys. Rev. Lett.* **2004**, *93*, No. 036805.

(60) Toher, C.; Sanvito, S. Efficient atomic self-interaction correction scheme for nonequilibrium quantum transport. *Phys. Rev. Lett.* **2007**, *99*, 056801.

(61) Garcia-Lastra, J. M.; Thygesen, K. S. Renormalization of optical excitations in molecules near a metal surface. *Phys. Rev. Lett.* **2011**, *106*, No. 187402.

(62) Freysoldt, C.; Rinke, P.; Scheffler, M. Controlling polarization at insulating surfaces: Quasiparticle calculations for molecules adsorbed on insulator films. *Phys. Rev. Lett.* **2009**, *103*, No. 056803.

(63) Atalla, V.; Yoon, M.; Caruso, F.; Rinke, P.; Scheffler, M. Hybrid density functional theory meets quasiparticle calculations: A consistent electronic structure approach. *Phys. Rev. B* **2013**, *88*, No. 165122.

(64) Linden, S.; Zhong, D.; Timmer, A.; Aghdassi, N.; Franke, J. H.; Zhang, H.; Feng, X.; Mullen, K.; Fuchs, H.; Chi, L.; Zacharias, H. Electronic structure of spatially aligned graphene nanoribbons on Au(788). *Phys. Rev. Lett.* **2012**, *108*, No. 216801.

(65) Liang, L. B.; Girao, E. C.; Meunier, V. Quasiparticle band gaps of graphene nanowiggles and their magnetism on Au(111). *Phys. Rev. B* **2013**, *88*, No. 035420.

(66) Liang, L. B.; Meunier, V. Electronic structure of assembled graphene nanoribbons: Substrate and many-body effects. *Phys. Rev. B* **2012**, *86*, No. 195404.

(67) Ruffieux, P.; Cai, J. M.; Plumb, N. C.; Patthey, L.; Prezzi, D.; Ferretti, A.; Molinari, E.; Feng, X.; Mullen, K.; Pignedoli, C. A.; Fasel, R. Electronic structure of atomically precise graphene nanoribbons. *ACS Nano* **2012**, *6*, 6930–6935.

(68) Yang, L.; Park, C.-H.; Son, Y.-W.; Cohen, M. L.; Louie, S. G. Quasiparticle energies and band gaps in graphene nanoribbons. *Phys. Rev. Lett.* **2007**, *99*, 186801.

(69) Becke, A. D. A new mixing of Hartree-Fock and density-functional theories. *J. Chem. Phys.* **1993**, 1372–1377.

(70) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215.

(71) Heyd, J.; Scuseria, G. E. Assessment and validation of a screened Coulomb hybrid density functional. *J. Chem. Phys.* **2004**, *120*, 7274–7280.

(72) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: “Hybrid functionals based on a screened coulomb potential”. *J. Chem. Phys.* **2006**, *124*, No. 219906.

(73) Brothers, E. N.; Izmaylov, A. F.; Normand, J. O.; Barone, V.; Scuseria, G. E. Accurate solid-state band gaps via screened hybrid electronic structure calculations. *J. Chem. Phys.* **2008**, *129*, No. 011102.

(74) Sumpter, B. G.; Meunier, V. Can computational approaches aid in untangling the inherent complexity of practical organic photovoltaic systems? *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 1071–1089.