REVIEW

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Nanoarchitectonics of Polymers at Interfaces

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The field of materials science is of paramount importance in the solution to societal issues, including energy, environmental, and biomedical problems. Polymer chemistry is a leading material science that has produced a number of practical materials. The development of nanotechnology for the control of ultrasmall structures and interface technology for the organization of polymer components has both made significant contributions to this field. This review, entitled "Nanoarchitectonics of Polymers at Interfaces," focuses on nanoarchitectonics and interface technologies to examine recent research trends on the design of functional polymeric materials. Three interface technologies are especially considered: i) the Langmuir–Blodgett (LB) technique, which allows for the orientation and hybridization of polymers at interfaces; ii) layer-by-layer (LbL) assembly, which allows for the construction of rational layered structures from polymers and other materials; and iii) on-surface synthesis, which uses nanotechnology to perform nanoarchitectonics of polymers on surfaces. The final section of the review discusses the trends and necessary future directions in "Nanoarchitectonics of Polymers at Interfaces" based on these research examples.

1. Introduction

Materials science holds the key to solving societal problems such as energy,[1] environmental,[2] and biomedical[3] issues. One of the goals of materials science is to enable the desirable creation of functional materials for specific purposes. Among various material sciences,[4] polymer chemistry is a leading field that produces practical materials. Polymers are rational materials made from different monomers as starting materials. Their length (molecular weight) can be precisely controlled.[5] Multicomponent polymers such as block and graft copolymers can also be produced.[6] The formation and dissociation of dynamic covalent bonds are also attracting attention.[7] Properties can be controlled by orientation and state of assembly.[8] Polymers with mechanical properties can also be used for clothing materials, molded objects, and advanced materials.[9] Conjugated polymers and photoresponsive polymers provide high electronic and photonic functions.[10] Polymers have also made a tremendous contribution to living systems, including DNA/RNA,[11] proteins,[12] and polysaccharides,[13] playing key roles in biological functions. Biopolymers, supported by precise structures, are considered to be the ultimate functional substances. Characterization of biopolymers and development of mimetic functions are being carried out.[14]

The great development of polymers as functional materials can be attributed to their synthesis, physicochemical analysis, and collaboration with biochemistry. In addition, two factors have made a major contribution. These are the development of nanotechnology, which can assess and control ultrasmall structures, and the development of interface technology, which can integrate polymers. The development of nanotechnology has made it possible to observe structures down to the atomic and molecular level[15] and to manipulate nanostructures,[16] making it possible to understand the physical properties of nanoscale.[17] As this knowledge has accumulated, the importance of controlling nanostructures in the creation of functional materials has become apparent.[18] In some cases, controlling the nanostructure is more important than synthesizing the material itself to achieve higher functionality. In addition, materials creations according to nanostructure controls have been paid continuous attentions with traditional self-assembly/self-organization[19] and emerging nanoarchitectonics.[20] The latter is general concept to build up functional materials from nano-units such as atoms, molecules and nanomaterials through combining various scientific and technological fields.

For more rational control of nanostructures and mesoscopic organizations, contributions by interfacial science are crucial. It is very useful to provide an interface, rather than a free space, to control nanostructures. At the interface, functional structures can be rationally constructed from polymers. In other words, the interface is a place where polymer nanoarchitectonics can be rationally developed. At the interface, various thin film fabrication methods are used to fabricate material structures. These include self-assembled monolayer (SAM),[21] Langmuir–Blodgett

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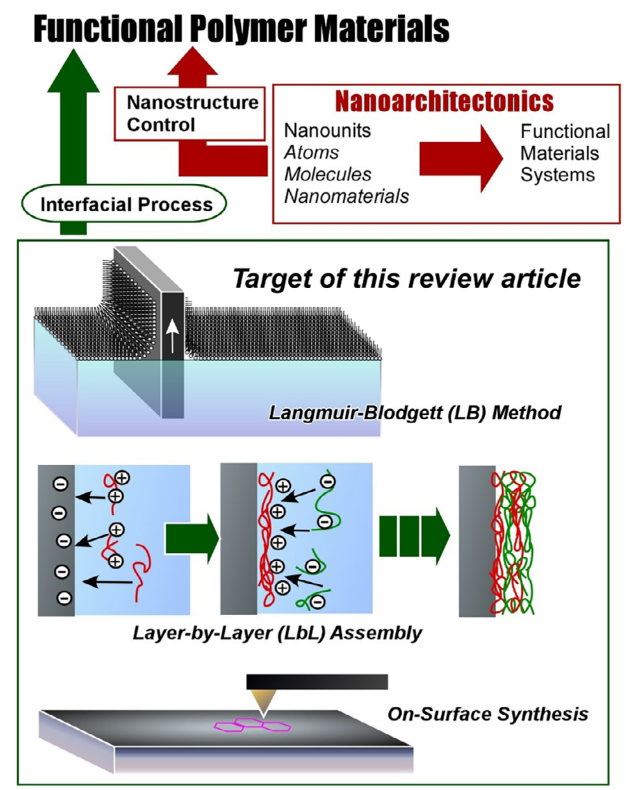

Figure 1. Outline and three major topics for nanoarchitectonics of polymers at interfaces in this review article.

(LB) method,[22] and layer-by-layer (LbL) assembly.[23] In particular, the LB method and LbL assembly are discussed as effective methods for nanoarchitectonics. In the LB method, the orientation of polymers can be controlled effectively in the monolayer (Langmuir monolayer) at the air–water interface. On the other hand, LbL assembly is an excellent method for integrating different polymers and different materials into layered structures. In addition to such traditional interfacial techniques, the creation of polymers and related two-dimensional materials on surfaces using nanotechnology has recently become popular. In a line of research called on-surface synthesis,[24] the nanoarchitectonics of polymer structures can be performed while observing molecular images with scanning probe microscopes.

This review, entitled "Nanoarchitectonics of Polymers at Interfaces," focuses on nanoarchitectonics and interface technologies to examine recent research trends on the design of functional polymeric materials. Three interface technologies are especially considered (**Figure 1**): i) the LB technique, which allows the orientation and hybridization of polymers at interfaces; ii) LbL assembly, which allows the construction of rational layered structures from polymers and other materials; and iii) on-surface synthesis, which uses nanotechnology to perform nanoarchitectonics of polymers on surfaces. In addition, this review also covers some challenging examples that do not fall into these categories. The examples discussed here are not necessarily the best in each field, but are typical examples to explore trends. Based on these research examples, the final section discusses the trends and necessary future directions in "Nanoarchitectonics of Polymers at Interfaces."

2. Langmuir–Blodgett (LB) Nanoarchitectonics

The orientation of functional polymers such as conjugated polymers has a significant effect on their performance. In addition, when considering applications in functional mechanisms and devices, the ability to form ultrathin films is advantageous.[25] From the dual perspective of the prospects for such functionality and the interest in fundamental polymer properties, Langmuir monolayers at the air–water interface and LB films have been used as a field of polymer research.[26] For controls of polymer properties and functions at gas–liquid interfacial media for LB techniques, three major factors, orientation control, molecular recognition, and thin film organization, are important. Such interfaces are actually nice media to control polymer orientations just by simple lateral pressure applications. Several examples are first introduced in this section. The air–water interface is also a media appropriate for molecular recognition and sensing because this interface provide encountering points between aqueous guest molecules and water-insoluble host monolayers. Some examples are next introduced. The LB method is surely useful to prepare nano-level thin films of various functional materials. In order to show such advantages, ferroelectric polymer for physical-chemistry investigations, cellulose nanocrystals for biochemistry emerging materials, and biomembrane mimics towered biomedical applications explained.

The orientation of conjugated polymers into supramolecular assemblies of a certain size is also an important challenge for the development of chemical sensors. Swager and co-workers investigated the conditions under which a conjugated polymer, poly(phenyleneethynylene), can be processed into a highly oriented film by the LB process and structurally assembled into fibril aggregates (**Figure 2**).[27] They found that several conditions are necessary for the monolayer to reassemble into a fibril structure. A low glass transition temperature, weak surface anchoring and a high-energy monolayer that can be stabilized by reorganization are required. The polymers form rigid structural units by assembling into aggregate structures. This means that after deposition, the monolayer reassembles into a highly anisotropic aggregated nanoscale fibril network. This conjugated electronic polymer network aggregates into structures with diameters of only a few tens of nanometers. It also becomes an interconnected structure with macroscale (centimeter) dimensions along the fibril axis. The chemical structure of the polymer units is also an important factor in the orientation pattern. Poly(phenyleneethynylene) molecules with methoxy acting as polar moieties with non-polar decyloxy groups are organized with the plane of the π system perpendicular to the air–water interface. On the other hand, poly(phenyleneethynylene) molecules with dioctylamide groups and polyether macrocycles are organized with the plane of the aromatic rings parallel to the interface. Thus, the orientation of the conjugated parts of the polymer also depends on the molecular designs. Tailor-made supramolecular nanoscale structures are important for the development of useful large biomolecules, chemical sensors, molecular electronic devices, etc. The monolayer system at the air–water interface has other advantages, such as the ability to induce docking of

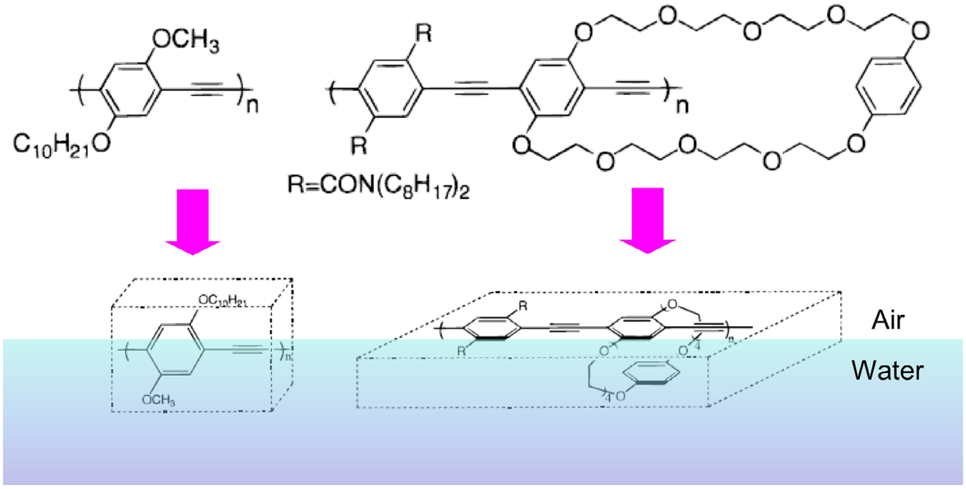

Figure 2. Orientation of the conjugated parts of the polymer, poly(phenyleneethynylene), depending on the molecular designs in their monolayer systems at the air–water interface. Reproduced with permission.[27] Copyright 1999, American Chemical Society.

biomolecules in the subphase and to create new structures or environments after deposition. Hybrid monolayer and multilayer assemblies are expected to lead to the development of various functional thin films.

Photoresponsive molecules and polymers are also attractive targets for LB research. In particular, azobenzene is a versatile photoresponsive unit, with simple rod-shaped photochromic molecules that have been widely studied. Azobenzene molecules have been linked to liquid crystal and polymer systems to develop motion functions. In a recent review, Seki has described photomechanical motion and morphological switching in block copolymer monolayers, dense brushes of azobenzene side-chain liquid crystal polymers, photoinduced mass transfer in azobenzene side-chain liquid crystal polymer films, and polymer motion due to Marangoni flow.[28] For more fundamental structural analysis of azobenzene polymers and their thin films, the LB method is a useful tool. Itoh and co-workers have studied the sum frequency generation spectra at the air–water interface for monolayers of polyvinyl alcohol derivatives containing azobenzene side chains (**Figure 3**).[29] The surface pressure dependence of the spectra was analyzed to elucidate the aggregate structure change of the monolayer accompanying the trans-cis isomerization of the azobenzene moiety. In the case of trans azobenzene polymers, the conversion of the alkyl group from an irregular to an ordered structure and the desorption of the polyvinyl alcohol moiety in the trans monolayer occur as the surface pressure increases. The orientation change of the long molecular axis of the azobenzene group to a state with less inclination with respect to the surface normal occurs in the early stage of the transformation of the trans monolayer from the less-condensed to the condensed state. In the orientation of the cis azobenzene moiety, the plane rotates about 90° around the C_2 axis and the axis remains parallel to the water surface. The rotation of the cis azobenzene group significantly changes the orientation of both the alkyl moiety and the polyvinyl alcohol moiety, leading to a condensed state. The photoinduced trans-cis isomerization of the azobenzene group has functions that can be applied to optical memory elements, optical switching devices, non-linear optical devices, liquid crystal alignment surfaces, etc. The LB method is useful for understanding the detailed orientation and structural changes of azobenzene and its surrounding groups that accompany isomerization.

The air–water interface is a medium in which the orientation and properties of not only elongated conjugated polymers but also molecular aggregates at the oligomeric level can be studied. Sakakibara et al. compared the association states of linear π-gelators in solution and at the air–water interface (**Figure 4**).[30] Typically, oligo(p-phenylenevinylene)-based π-gelators self-assemble into entangled fibers in solution, with the molecules oriented perpendicular to the long axis of the fibers. However, it remains difficult to orient the gelator molecules parallel to the long axis of the 1D structure. At the air–water interface, oligo(p-phenylenevinylene)-based π-gelators form aligned nanorods in which the gelator molecules are reoriented parallel to the long axis of the rods. Near-field scanning optical microscopy confirmed that the change in molecular orientation leads to distinct excited state properties upon localized optical excitation. Excitation of the fibers in the entangled network formed in solution produces fluorescence along the fibers. In such fibers, long-range excitation energy transfer occurs and fluorescence is largely quenched. Meanwhile, at the air–water interface, aligned rods show modulation of fluorescence along individual rods and between closely packed rods. Localized regions of fluorescence were observed when aligned rods were excited. Large fluorescence enhancement occurs in the aligned nanorods. Thus, entangled gel fibers with vertically aligned molecules are favorable for excitation energy transfer. LB nanorods with parallel molecular alignment may be favorable for charge transport. These results demonstrate the importance of controlling the molecular organization and nanoscale morphology of self-assembled architectures to control the excited state properties. This is also useful for efficient sensing and imaging applications.

The air–water interface is not only a place of orientation control, but also a place of recognition of molecules and ions.[31] The air–water interface is useful as a site for capturing water-soluble guest molecules and ions by water-insoluble host molecules. Fujimori and co-workers investigated the metal capture and

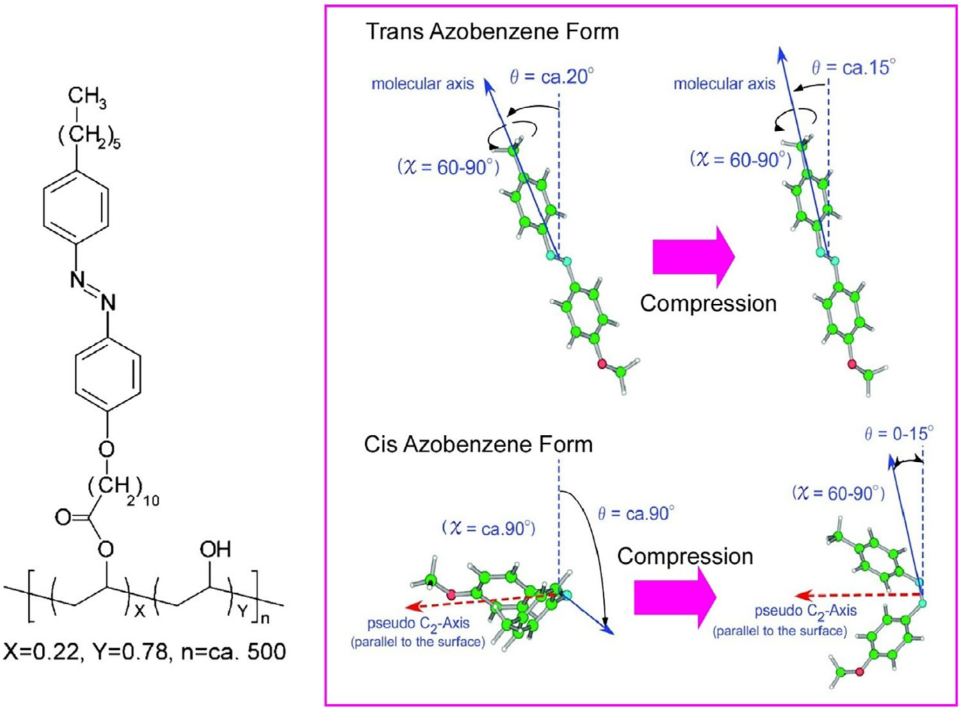

Figure 3. Monolayers of polyvinyl alcohol derivatives containing azobenzene side chains for their investigation by the sum frequency generation spectra at the air–water interface: (left) polymer chemical structure; (right) proposed conformational changes of the azobenzene moiety in trans and cis form upon compression. Reproduced with permission.[29] Copyright 2007, American Chemical Society.

desorption ability and selective metal removal properties of an interfacial molecular film of a highly ordered copolymer with bulky azacalixarene rings (**Figure 5**).[32] The synthesized copolymer consists of azacalixarene rings and repeating units based on crystalline polyethylene glycol chains. The azacalixarene rings exhibit metal trapping ability because the lone pairs of electrons of the abundant nitrogen atoms are oriented inside the rings, forming a negative electric field. A monolayer of this copolymer on the water surface was able to collect various metal ions from the subphase, and in particular to capture monovalent ions. Metal cations are incorporated into the azacalixarene rings by weak interactions with the applied electric field. The trapped ions could be desorbed or retrieved by simple sonication. Taking advantage of the fact that the monolayer can capture metals as soon as it begins to spread, this method may be applicable to water surfaces with a large surface area. It is expected that rare metals and rare earth metals can be selectively recovered from seawater with this method.

Ferroelectric polymers are flexible, transparent, and lightweight. They are therefore promising for wearable electronic and optical applications. To realize the full functional potential of polarization-enabled devices, large-scale fabrication of polymer thin films with well-controlled polar orientation is required. Hong and co-workers have successfully fabricated highly ordered crystalline poly(vinylidene fluoride-trifluoroethylene) nanowire films by interfacial epitaxy with 1T′-ReS$_2$ using the LB technique (**Figure 6**).[33] They exploit the interfacial epitaxial relationship with the anisotropic van der Waals material 1T′-ReS$_2$. Upon thermal treatment, the uniform LB film self-assembles into crystallographically aligned, close-packed nanowires with the underlying ReS$_2$ with an out-of-plane polarization axis. Unlike polycrystalline or polymorphic poly(vinylidene fluoride-trifluoroethylene) films, densely packed poly(vinylidene fluoride-trifluoroethylene) nanowire films have structural properties such as high crystallinity and enhanced out-of-plane polar alignment due to the interfacial epitaxial relationship, which are highly advantageous for energy-efficient device applications, e.g., enabling very high non-volatile current switching ratios. Another advantage of this approach is that it can be easily scaled to wafer-scale fabrication. This could provide an important basis for the realization of ferroelectric polymer/2D van der Waals heterostructures for lightweight, low-power and portable nano- and optoelectronics.

Cellulose nanocrystals are sustainable nanoparticles derived from inexpensive renewable resources, and their effective use is of great societal importance.[34] Cellulose nanocrystals are ideal nanoparticles for creating anisotropic surfaces and nematic structures. The creation of oriented structures from cellulose nanocrystals has attracted much attention. Cellulose nanocrystals interact strongly with amine-functionalized polyhedral oligomeric silsesquioxane at the oil–water interface. The assembly of these two components also becomes a cellulose nanocrystal surfactant. This property makes them suitable for use in the LB method. Wang and co-workers demonstrated that the strategy of nanoparticle surfactant formation at the liquid–liquid interface can be combined with the LB method to form cellulose nanocrystal surfactant monolayers (**Figure 7**).[35] First, an aqueous solution of cellulose nanocrystals and a chloroform solution of polyhedral oligomeric silsesquioxane are placed in a Langmuir trough, resulting in the formation of a

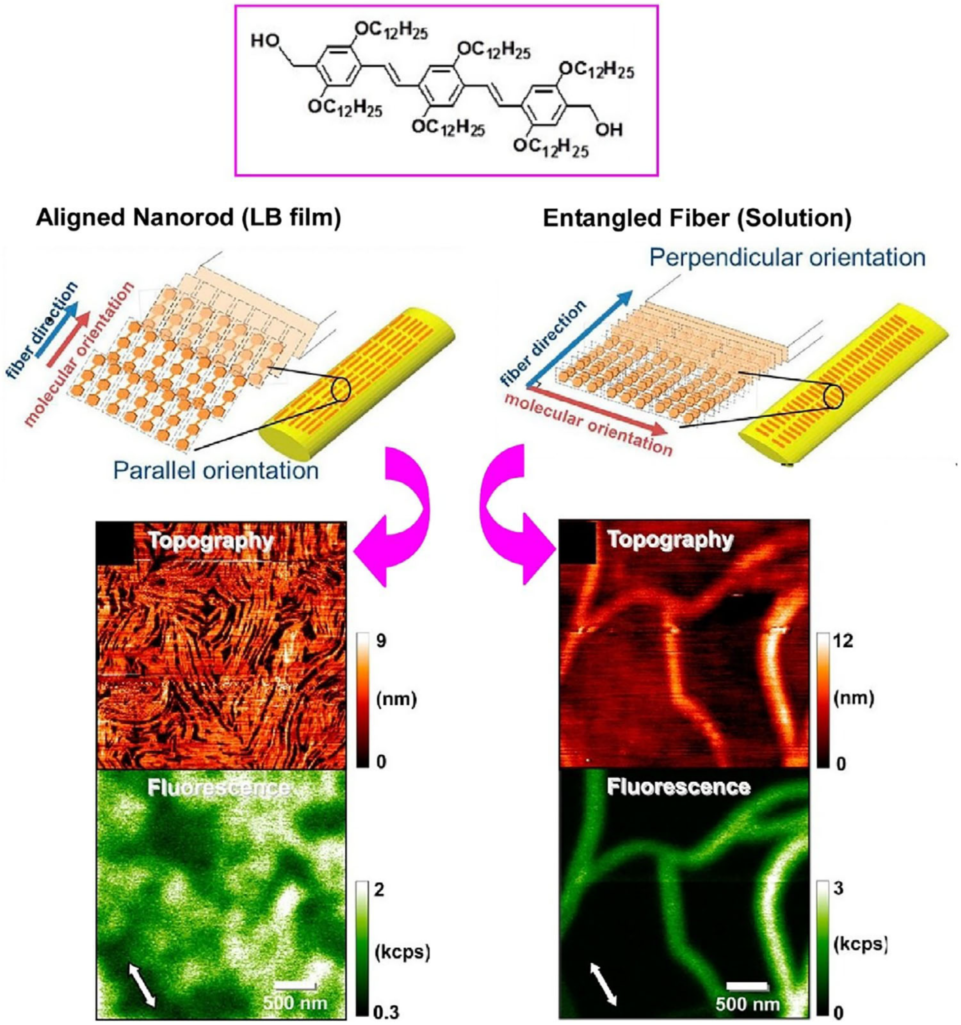

Figure 4. Assembling structures of oligo(p-phenylenevinylene)-based π-gelator of aligned nanorods formed in LB film (left) and entangled fibers formed in solution (right): proposed assembly model, topological image and fluorescence image upon near-field scanning optical microscopy. Reproduced with permission.[30] Copyright 2014, American Chemical Society.

cellulose nanocrystal surfactant monolayer. Upon compression, a disorder-to-order transition of the cellulose nanocrystal surfactant arrangement occurs. During this transition, the packing of the cellulose nanocrystal surfactant within the generated monolayer changes from a network-like pattern to an ordered arrangement. This approach can be generalized to allow nanoparticles to interact with polymer ligands with complementary functionalities to form nanoparticle surfactants at the liquid–liquid interface, making it a versatile method for producing different types of nanoparticle surfactant monolayers.

The LB method, which allows flexible construction of lipid membranes, is useful as a model system for biological cell membranes. Research into antibiotic-resistant bacteria is an important goal. Resistance of Gram-negative bacteria to various antibiotics, such as penicillins and quinolones, is increasing and has become a serious global health problem. In response, the use of large cationic antimicrobial peptides, such as polymyxins, is seen as a new strategy to combat antibiotic resistance. Su et al. constructed a model bilayer of di[3-deoxy-D-mannooctulosonyl] lipid A (Kdo$_2$ lipid A) on a β-Tg-modified gold (111) surface to mimic the outer membrane of Gram-negative bacteria (**Figure 8**).[36] A model bilayer of the Gram-negative bacterial outer membrane, consisting of lipid A and 1,2-dimyristoyl-sn-glycero-3-phosphoethanolamine, was constructed on a β-Tg-modified gold (111) single crystal surface by combining the LB method and the Langmuir–Schaefer (LS) method. The properties of the model bilayer and its interaction with polymyxin were studied using electrochemical and spectroscopic methods. The interaction of the polymyxin with the bacterial membrane involves the charging of the outer lipid membrane, which is provided by the negatively charged phosphate and carboxylate groups. The Mg^{2+} competition between the polymyxin and the positively charged lipopeptide is key. The effect of the positively charged peptide on the outer sphere of the bacterial membrane was well interpreted to be an important factor. In other words, the results show that the antibacterial activity of polymyxin depends on the membrane potential of the model bilayer membrane. Such findings provide useful information for the development of new antibiotics.

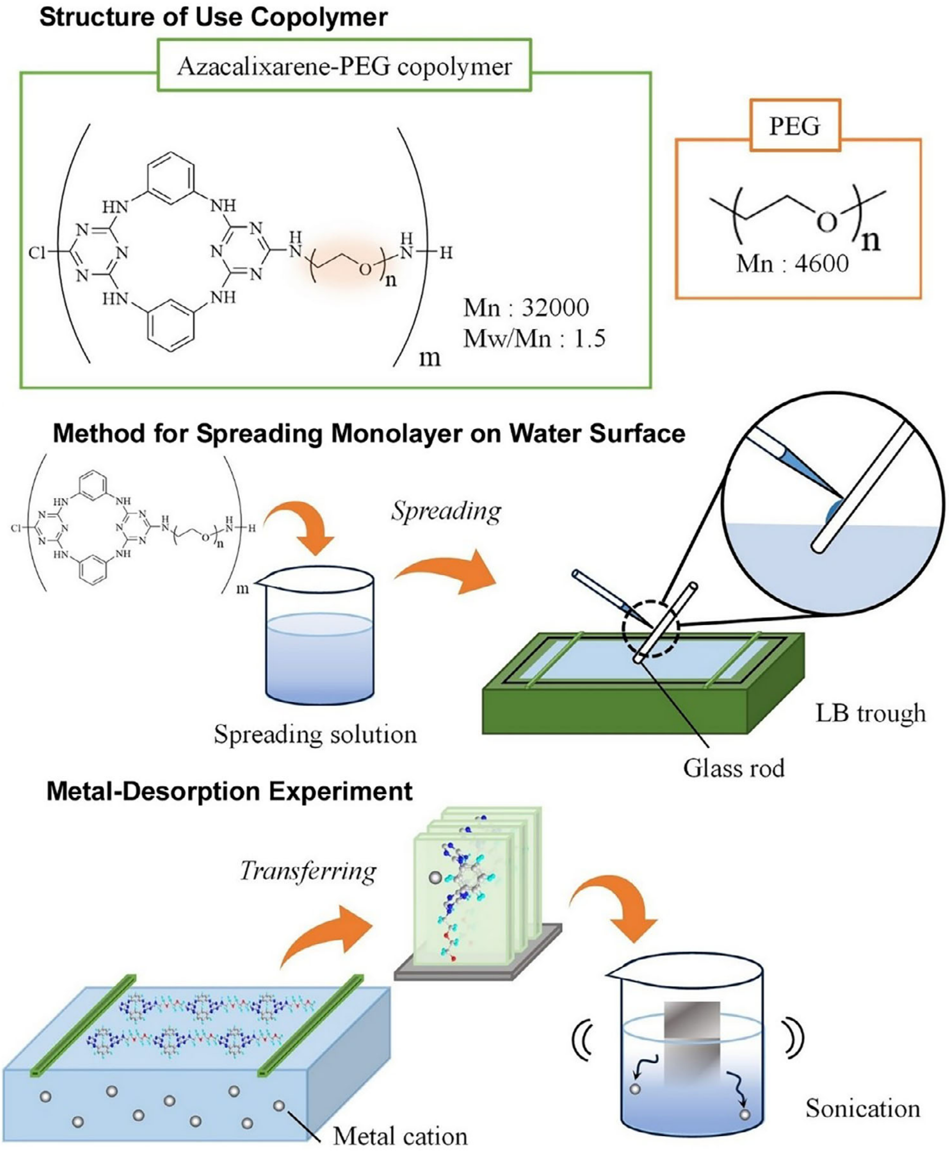

Figure 5. Selective metal removal properties of an interfacial molecular film of a highly ordered copolymer with bulky azocalixarene rings: structure, method for spreading monolayer on water surface, and metal-desorption experiment. Reproduced with permission.[32] Copyright 2024, Oxford University Press.

Antibacterial surfaces can be designed in two main ways: passive surfaces that repel bacteria by altering the wettability of the surface, and active surfaces that have bactericidal properties by disrupting cell membranes on contact. Effective antibacterial strategies that combine these properties have attracted attention. This requires the development of surfaces with dual antibacterial functions. Palivan and co-workers have developed a nanotextured surface resulting from the phase separation of two different amphiphilic block copolymers that provide an efficient dual function against bacterial growth (**Figure 9**).[37] A thin hybrid film of immiscible amphiphilic block copolymers exerts dual antibacterial and antifouling functions to efficiently reduce *Escherichia coli* biofilms. This approach combines the inherent antifouling properties of polyethylene oxide as the hydrophilic domain of one copolymer with the antibacterial effect of a peptide covalently attached to the hydrophilic domain of the second copolymer. The planar film is transferred to a solid support by LB and LS techniques to create a textured motif with a phase-separated structure. An antibacterial peptide is then covalently attached to one of the specially functionalized copolymers. The combination of both copolymers on the same surface significantly reduced *E. coli* biofilm formation and effectively eradicated the bacteria during short-term incubation. Hybrid films with covalently attached antimicrobial peptides significantly inhibited bacterial growth. Combining both endogenous and exogenous functionalities of these hydrophilic blocks showed a synergistic effect in preventing bacterial growth and biofilm formation. Such hybrid polymer surface strategies can realize a wide range of combinations of biomolecules such as enzymes, proteins, DNA and antibodies, or nanoassemblies such as nanoparticles and micelles.

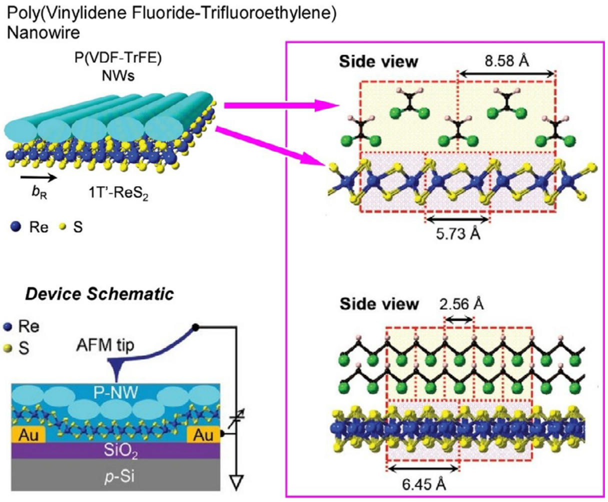

Figure 6. Highly ordered crystalline poly(vinylidene fluoride-trifluoroethylene) nanowire films by interfacial epitaxy with 1T'-ReS$_2$ using the LB technique. Reproduced with permission.[33] Copyright 2021, Wiley-VCH.

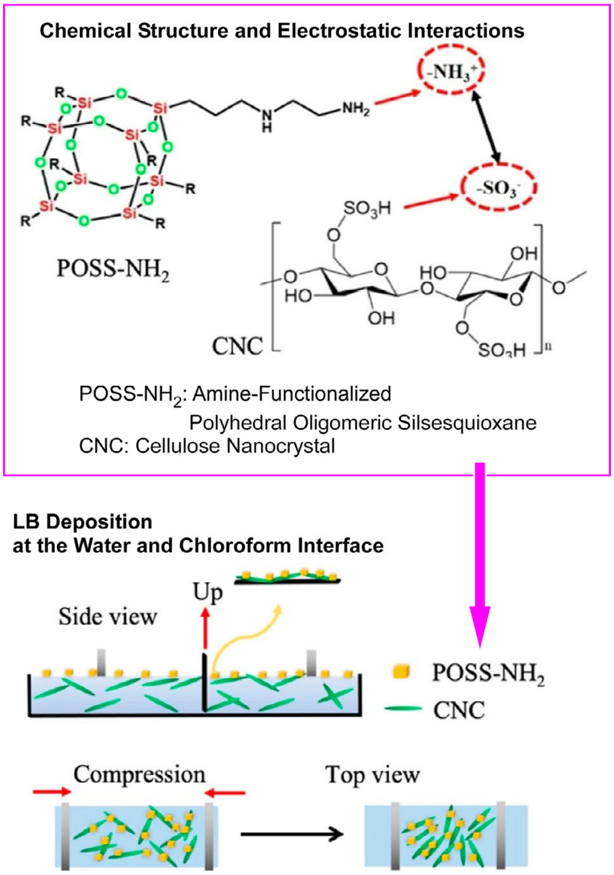

Figure 7. Nanoparticle surfactant formation at the liquid–liquid interface combined with the LB method to form cellulose nanocrystal surfactant monolayers with the aid of polyhedral oligomeric silsesquioxane with amino group: chemical structure, electrostatic interaction, and LB deposition. Reproduced with permission.[35] Copyright 2022, American Chemical Society.

Multifunctional surfaces are expected to provide a new approach to achieve dual antifouling and antibacterial effects in thin films suitable for applications such as dental implants and biosensors.

As mentioned above, Langmuir monolayers at the air–water interface and LB films are important methods for polymer nanoarchitectonics. The presented examples extract tendencies of polymer science and technology with the LB technique. As seen the initial few examples, fundamental aspects such as orientation controls by surface pressures and molecular recognitions at the air–water interface are active research matter. It may reflect long history of the LB method and its strength in elucidation of fundamental physical properties. In parallel, application-oriented research efforts are continuously made. Many studies have shown that such properties have great potential for device applications, resource recovery, medical applications, and more. In particular, the ability to form ultrathin films at the molecular level in an aqueous environment makes them highly useful as models or mimics of biological membranes. There are high expectations for their development in medical applications related to cell membranes.

3. Layer-by-Layer (LbL) Nanoarchitectonics

While the LB method has the advantage of controlling the orientation within a molecular monolayer, the LbL assembly is good at forming different layered structures at the interface. The main feature of the LbL method is that it can freely assemble different substances, such as inorganic substances like colloidal particles and biomolecules like proteins. However, the basic method of LbL is the alternating adsorption phenomenon of polyelectrolytes. The contribution of polymers is universal in LbL science. The LbL method is considered to be a powerful method for polymer interface nanoarchitectonics. This section presents some examples of LbL assembly research, focusing mainly on functional polymers including several new methods. One of the distinct advantages of LbL assembly is its flexibility in their designs, methods, and applications, which continuously creates new challenges in the corresponding fields. Such features are mainly indicated in this section. Although the LbL assembly is traditionally based on non-covalent electrostatic interactions, such very basic matters are even re-examined for new challenges. Examples of intentional charge controls and rational introduction of covalent bonding in LbL processes are mentioned in the first few examples. Of course, a wide applicability of this method to several sensor usages, chemical sensor and biosensor, are the next demonstrated with advantages of controlled layer designs. At the last several examples in this section, new challenges with expansion of LbL concepts are mentioned, in which electrochemical controls of stepwise layering are used as new tools.

Nanofilms made by LbL assembly of polyelectrolytes are important materials for various applications. However, because it involves a charge neutralization process of electrostatic interactions, the interior cannot retain excess charges along the polymer chains. This results in a low net charge density. Matsusaki and co-workers have successfully produced LbL nanofilms with retained positive charges using an approach that introduces covalent bond formation (**Figure 10**).[38] In this method, azide and alkyne groups were partially grafted onto poly-L-lysine, a polycation. Using copper-catalyzed azide-alkyne cycloaddition and

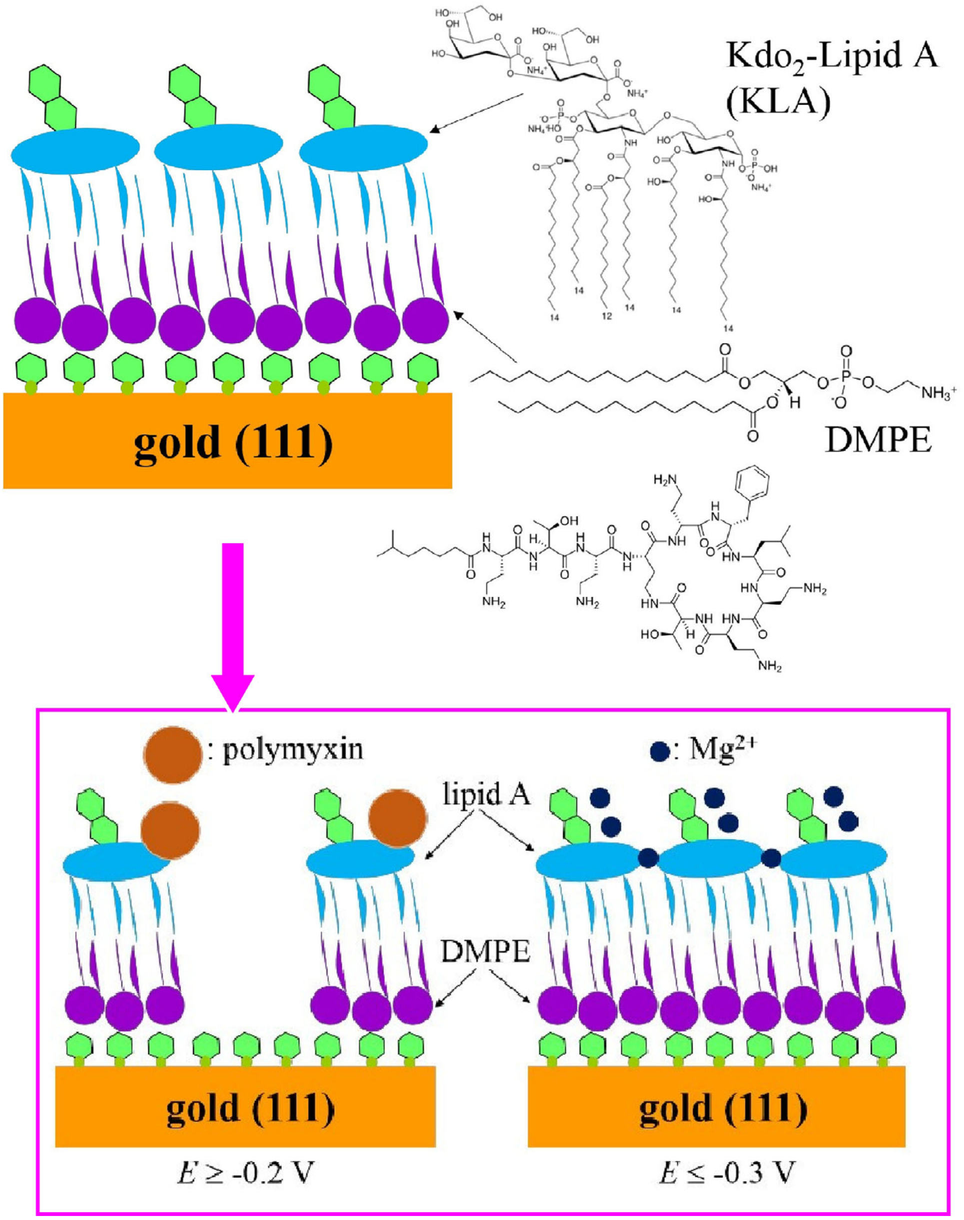

Figure 8. A model bilayer of di[3-deoxy-D-mannooctulosonyl] lipid A (Kdo2 lipid A) on a β-Tg-modified gold (111) surface to mimic the outer membrane of Gram-negative bacteria for investigation on interaction of the polymyxin with the bacterial membrane involving Mg^{2+} competition. Reproduced with permission.[36] Copyright 2024, American Chemical Society.

the LbL method, they produced nanofilms in which all the individual layers were covalently bonded. After the formation of stable triazoles, the degree of ionization of the amino groups could be tuned by adjusting the pH. The stable covalent bonds between the individual layers improved the robustness of the nanofilms. The resulting nanofilms, which have positive charges both inside and on the surface with a high charge density, are pH-responsive and have excellent absorption properties for negatively charged molecules. This type of nanofilm has great potential for applications in biomedical and environmental sensing, diagnostics, and filtration of nanomaterials. This methodology can also be extended to other click reactions. Fully monocharged LbL nanofilms are expected to be useful for biomedical applications.

As an LbL membrane with a covalent bond structure between the layers, Hegaard and Thormann systematically investigated the effects of composition, salt concentration and ion specificity on the pH response of covalently cross-linked chitosan and alginic dialdehyde multilayer films (**Figure 11**).[39] LbL multilayer films with different chitosan to alginic dialdehyde ratios were obtained by the LbL assembly process at pH 3 and 6. The swelling response to increasing ionic strength was consistent with that observed for polyzwitterionic and weak monocomponent polyelectrolyte films. It was dependent on the composition, pH and ion specificity of the multilayer. The pH and ionic strength dependent swelling behavior is highly dependent on the ion pairing effect. These results can serve as inspiration for the design of

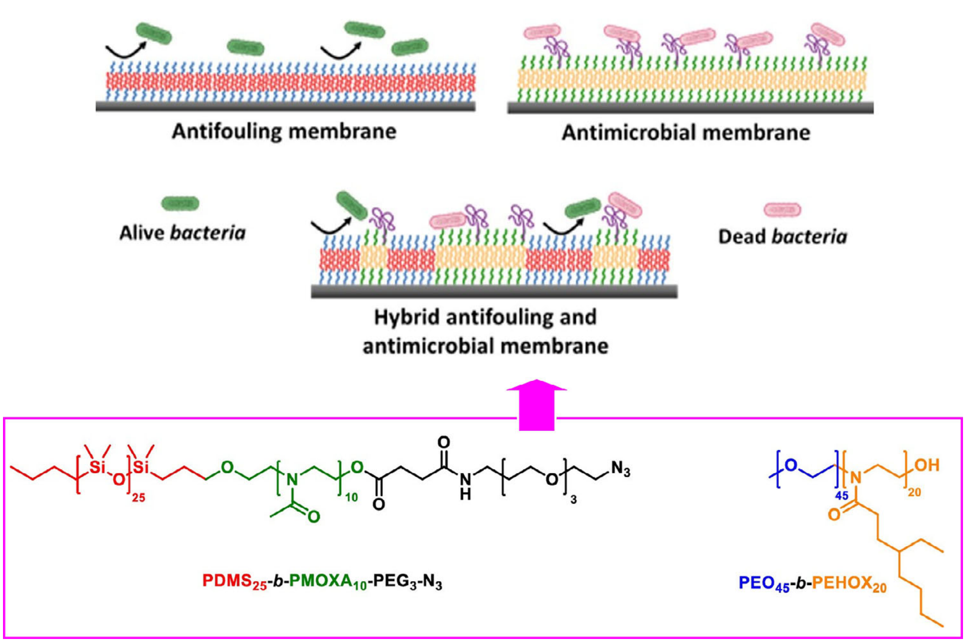

Figure 9. A nanotextured surface resulting from the phase separation of two different amphiphilic block copolymers with an efficient dual function against bacterial growth, where the hybrid film of immiscible amphiphilic block copolymers exerts dual antibacterial and antifouling functions to efficiently reduce *E. coli* biofilms. Reproduced with permission.[37] Copyright 2024, American Chemical Society.

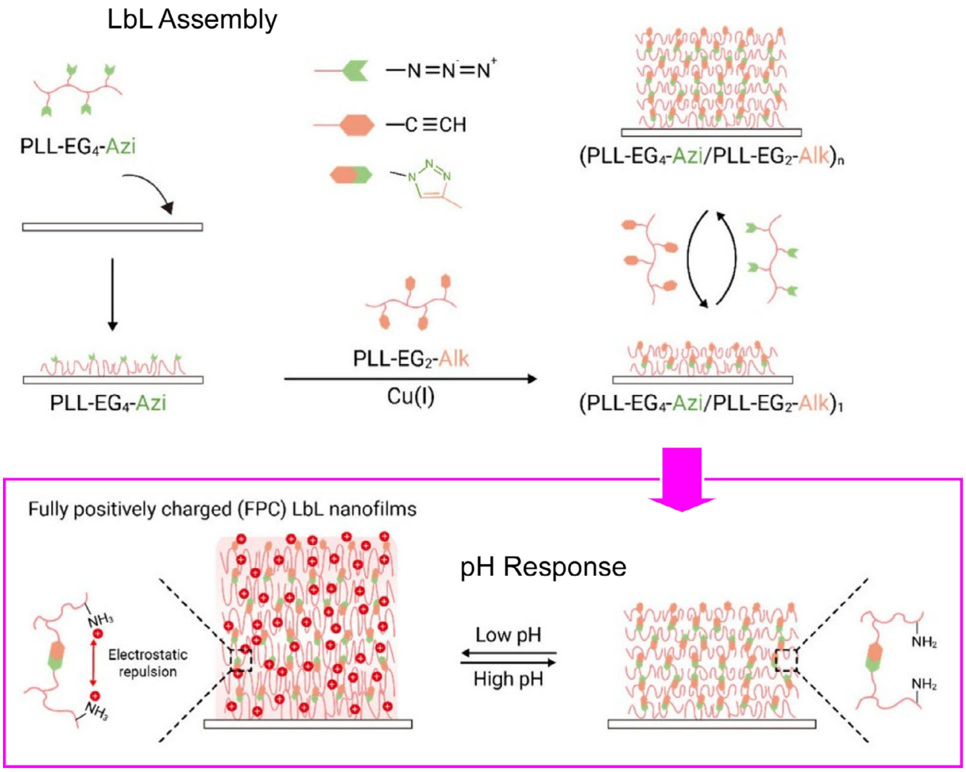

Figure 10. LbL nanofilms with retained positive charges using an approach that introduces covalent bond formation, in which all the individual layers were covalently bonded though copper-catalyzed azide-alkyne cycloaddition for pH-responsive functions. Reproduced with permission.[38] Copyright 2024, American Chemical Society.

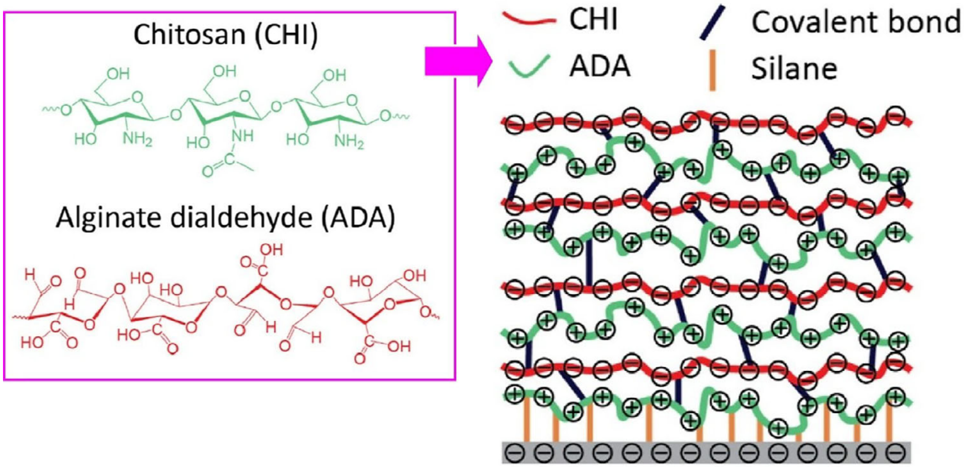

Figure 11. A covalently cross-linked chitosan and alginic dialdehyde LbL multilayer film. Reproduced with permission.[39] Copyright 2023, American Chemical Society.

responsive multilayer films with desired functions under specific environmental conditions.

Jewrajka and co-workers reported the preparation of high performance molecular selective membranes by non-electrostatic adsorption of polyelectrolytes onto polyvinylidene fluoride substrates with negative zeta potentials followed by electrostatic LbL assembly (**Figure** 12).[40] When the first layer is poly(sodium styrenesulfonate), the LbL-assembled membrane contains free $-SO_3$ groups, resulting in high rejection of Na_2SO_4 and low rejection of $MgCl_2$. The trend of salt rejection is reversed when the first layer is quaternized polyvinylimidazole. The key finding of this work is the knowledge that the nature of the polyelectrolyte used in the construction of the first layer of the LbL sequence determines the overall performance of the membrane. This approach could provide a methodology for the construction of low fouling, high performance membranes for dye and salt fractionation by LbL membranes.

Poly(3,4-ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) is a widely used conductive polymer. It has the characteristics of good water solubility, harmless environmental stability and excellent room temperature conductivity. Taking advantage of these properties, it is used for chemiresistive sensing of ammonia. Zhou and co-workers developed an ammonia sensor by incorporating alkalized cellulose nanofibers into a host PEDOT:PSS matrix by LbL assembly (**Figure** 13).[41] This ammonia sensor exhibited a low experimental detection limit, short response/recovery time, excellent reproducibility, and long-term stability and selectivity. The NH_3 sensing mechanism of the sensor is based on direct charge transfer during gas–solid interaction. When the hole-conducting PEDOT in the sensing film reacts with the electron-donating NH_3 molecules, the electron transfer from NH_3 to PEDOT increases the degree of delocalization of the conjugated π electrons along the PEDOT backbone. The incorporation of alkalized cellulose nanofibers significantly improved the performance. In particular, the abundance of –OH groups promoted molecular NH_3 adsorption and electron release from NH_3. Charge transfer was also enhanced due to the increased roughness of the film. These factors improved the sensitivity and selectivity. The developed sensor was flexible and performed well at different bending angles and bending times. The methodology presented here has broad prospects in the field of wearable optoelectronic systems.

Pesticides have adverse effects on human health. Detection of pesticide residues is important for food safety management and environmental protection. Single-stranded oligonucleotides, called aptamers, can selectively bind to target pesticide molecules with high affinity, making them useful as sensing elements. Skorb and co-workers have developed a novel biosensor for pesticides by incorporating aptamer oligomers into a soft polymer matrix consisting of an LbL film of polyethyleneimine and polystyrene-co-phenylenediamine (**Figure** 14).[42] This is an aptamer-based electrochemical biosensor for the detection of glyphosate, a commonly used pesticide. The specific interaction of the oligonucleotide with the pesticide leads to the accumulation and concentration of pesticide molecules near the electrode surface. This allows easy and simple electrochemical detection, both qualitatively and quantitatively. The structure and composition of the oligonucleotides can be precisely tailored to each target molecule, making this a versatile method.

Although electrostatic interactions are often used as the driving force in LbL assembly, various interactions and chemical reactions have been used. Li et al. developed a novel method called electrochemical coupling LbL (ECC-LbL) assembly (**Figure** 15).[43] In the ECC-LbL method, molecular thin films are sequentially immobilized on electrodes by electrochemical coupling reactions. The dimerization of *N*-alkylcarbazole was chosen as a coupling reaction that can be triggered by electrochemical stimulation. *N*-alkylcarbazole and its dimer have high hole transport mobility, allowing the electrochemical signal to be transferred to the top layer of the film from the electrode. This method allows the stacking of functional units such as porphyrins, fullerenes, and fluorenes in both homo- and heteroassemblies. Thin films of desired thickness and designable sequences can be covalently immobilized, ensuring efficient electronic interactions between the layers. The process is clean and requires no reagents. It is therefore particularly suitable for building covalently bonded, layer-controlled thin films on sensitive device surfaces. Another advantage of this approach is that the di-*N*-alkyl carbazoles obtained are

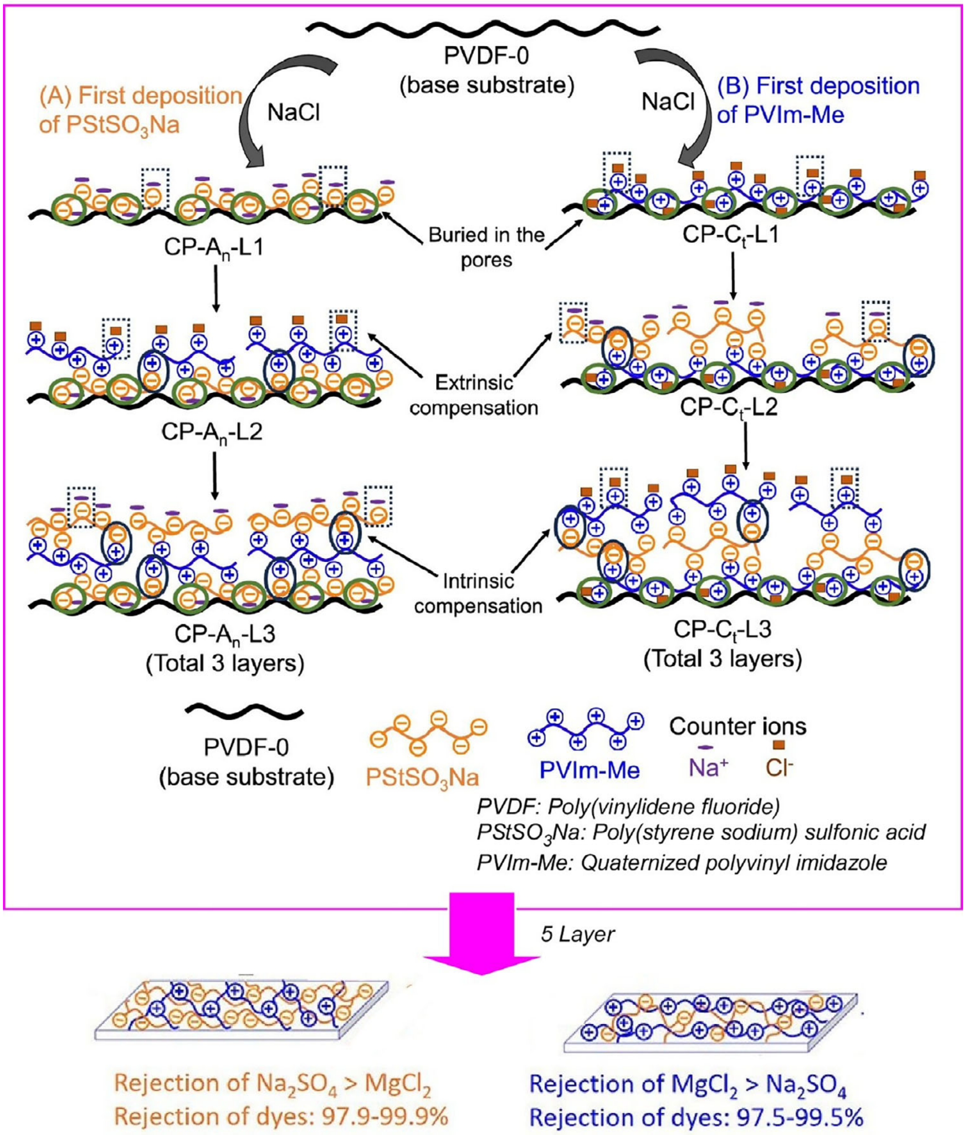

Figure 12. Preparation of high performance molecular selective membranes by non-electrostatic adsorption of polyelectrolytes onto polyvinylidene fluoride substrates with negative zeta potentials followed by electrostatic LbL assembly, where the nature of the polyelectrolyte used in the construction of the first layer of the LbL sequence determines the overall performance of the membrane. Reproduced with permission.[40] Copyright 2024, American Chemical Society.

transparent in the visible light region, so that the optical or electrical properties of the active moieties in the film are not compromised. As a functionalization of ECC-LbL, the photovoltaic function of a prototype p/n heterojunction device was demonstrated. As a thin film optoelectronic device, an attractive potential application of heterojunction films, their photovoltaic properties was investigated. This approach makes it possible to ensure efficient electronic communication between the layers. Since the coupling reactive sites used in ECC-LbL are independent of the functional units, this method can be applied when many types of organic functional groups are present. Therefore, the ECC-LbL approach has the potential to be used in various types of organic devices. It is a powerful method for constructing robust and well-designed organic layered structures.

Electrochemical methods to covalently link molecular units from the surface are being developed as a new polymer nanoarchitectonics. Attempts are being made to synthesize crystalline polymers with well-defined orientation states and two-dimensional crystal sizes exceeding micrometers. This is essential to realize the best physical properties of polymer materials. It can be a way to approach the physical limits of density, modulus, conductivity, etc., which is one of the ultimate goals of polymer science. Hong, Li and co-workers proposed a method to obtain crystalline polymers with well-defined thickness and molecular length by an electrochemical iterative approach (**Figure 16**).[44] This method will demonstrate the creation of crystalline polymer monolayers to approach the physical limits of polymer electronic materials. It will also challenge the synthetic iterative limit of

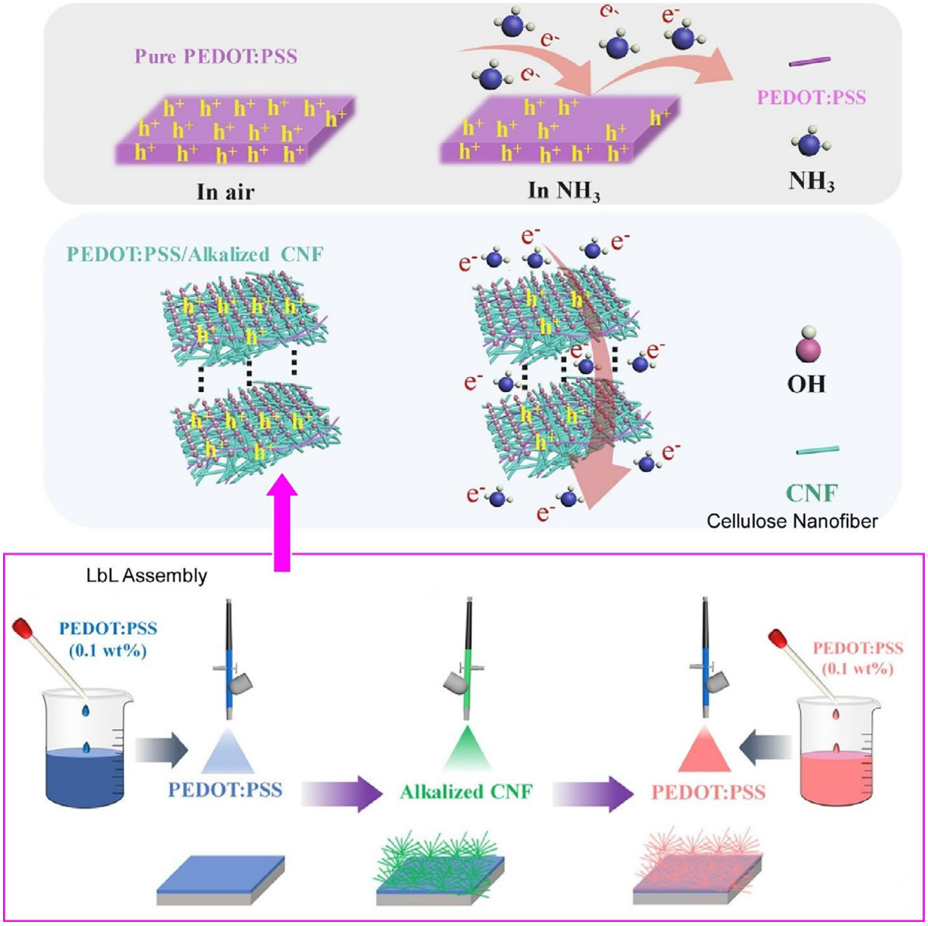

Figure 13. An ammonia sensor by incorporating alkalized cellulose nanofibers into a host PEDOT:PSS matrix by LbL assembly, in which the electron transfer from NH_3 to PEDOT increases the degree of delocalization of the conjugated π electrons along the PEDOT backbone upon reaction of the hole-conducting PEDOT with the electron-donating NH_3 molecules. Reproduced with permission.[41] Copyright 2023, American Chemical Society.

isolated ultra-long chain polymers. In this method, starting from a self-assembled monolayer as a template and repeating monomer reaction, the theoretically densest crystalline polymer monolayer is synthesized by solid-phase iterative electrosynthesis. It can be a way to synthesize crystalline unipolymer monolayers with exceptional ultra-high modulus and high conductivity. The polymer monolayers are fully stretched with vertical and unidirectional orientation, approaching the highest theoretical density, modulus, and conductivity. They also represent a strategy for achieving macroscopic 2D crystalline materials from polymers that are extremely difficult to crystallize. The scalable and programmable electrosynthesis of the polymers allows the synthesis of 2D crystalline materials on rigid or flexible conductive substrates at the centimeter scale and beyond. The polymers produced also exhibit bias- and length-dependent multiple charge states and asymmetric negative differential resistance effects. They are expected to be useful in miniaturized and portable optoelectronic applications.

Such a methodology is also applicable to the nanoarchitectonics of polymers containing multiple monomer components. Li and co-workers reported the rapid sequence-controlled electrosynthesis of organometallic polymers with elaborate insertion of several different monomers (**Figure 17**).[45] The reactions selected for iterative electrosynthesis are oxidative self-coupling of N-phenylcarbazolyl and reductive self-coupling of vinyl on pyridine coordinated to the metal core between two monomers. The electrosynthesis is initiated by oxidative coupling of carbazolyl between the monomer in solution and the pendant of the complex self-assembled on ITO-coated glass. The electrosynthesis is carried out by oxidative and reductive C–C coupling with a reaction time of 1 min each. It is operated by switching between reductive and oxidative coupling with alternating solutions containing the same or different monomers. The polymer synthesis can be monitored by both UV–vis spectroscopy and cyclic voltammetry. Once the multi-component monomer has been synthesized, it can also be encoded into sequence-controlled organometallic polymers. Highly efficient electrosynthesis with the potential for automated production is also expected. The high-efficiency reactions, ease of cleaning and purification, and real-time monitoring could be integrated with computer control to enable mechanized and automated processes for the nanoarchitectonics design of desired polymer structures.

A major advantage of the LbL method is that it can be applied to a wide variety of components, but the examples above show that even if the components are limited to polymers

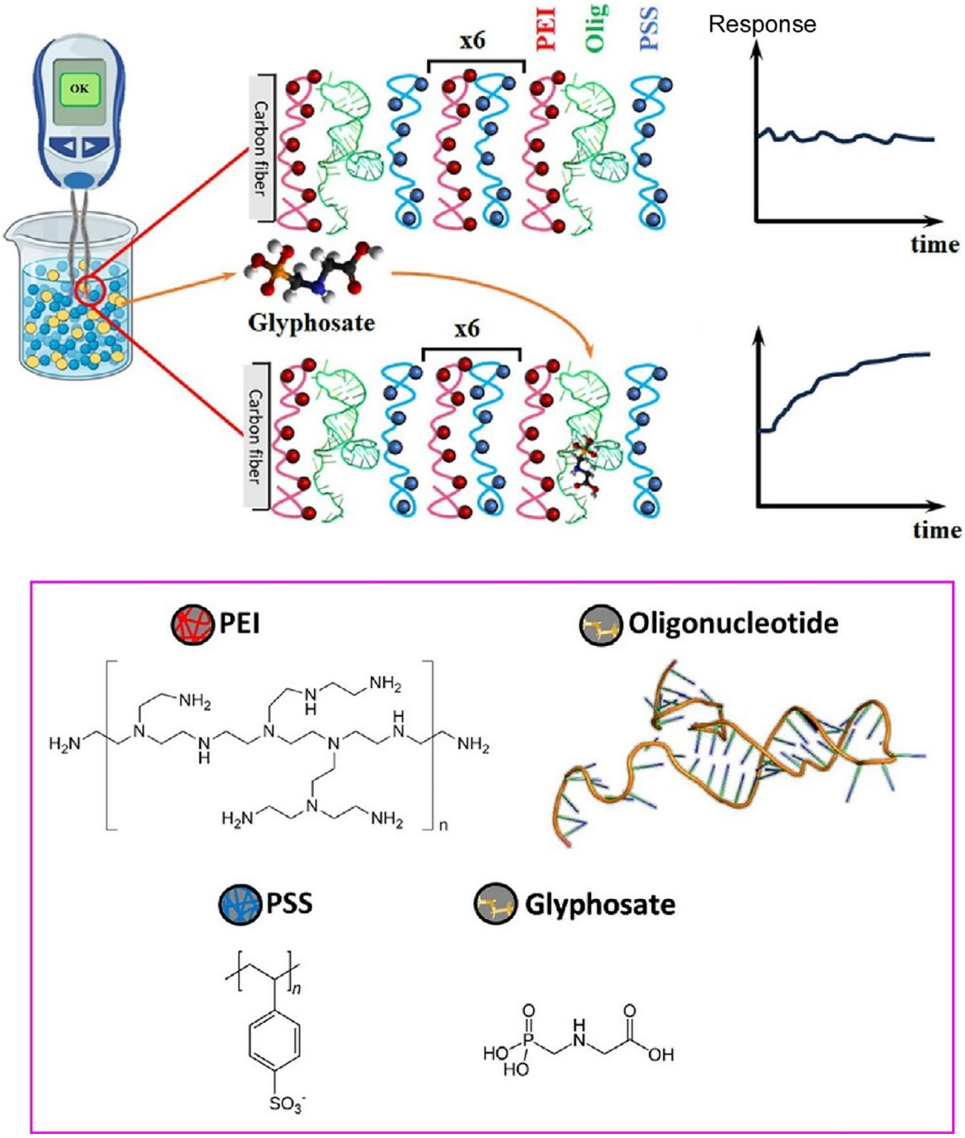

Figure 14. A biosensor for the detection of glyphosate, a commonly used pesticide, constructed by incorporating aptamer oligomers into a soft polymer matrix consisting of an LbL film of polyethyleneimine and polystyrene-co-phenylenediamine. Reproduced with permission.[42] Copyright 2023, American Chemical Society.

(polyelectrolytes), there is still ample potential for functional exploration. The presented examples indicated that the LbL assembly has two different tendencies, re-exploration on fundamental methodologies and challenging to explore new techniques. This feature may come from rather young nature of the LbL research as compared with the LbL method. Not limited to the conventional assembling process using electrostatic interactions, interlayer fixation using covalent bonds is explored. This approach is especially useful for applications where sufficient mechanical strength is required. Furthermore, the methodology of creating covalent bonds stepwise from the surface may lead to new polymer synthesis methods. This opens up new possibilities for polymer nanoarchitectonics in interfacial environments.

4. On-Surface Synthesis Nanoarchitectonics

The example above shows a method for stretching a polymer vertically from a surface. Meanwhile, methods are also being developed to create polymer structures on two-dimensional surfaces and to accurately evaluate their mechanisms and structures. For example, in the field of on-surface synthesis, the reactant structures on the surface can be evaluated at the atomic and molecular level using a probe microscope. Examples with visual images of molecular-level polymer structures are shown in this section. To impress high potentials of this emerging research field, this sections exemplified various visual images. Following one pioneer example of tip-initiated polymerization, on-surface syntheses for covalent chain manipulation, non-linear (circular)

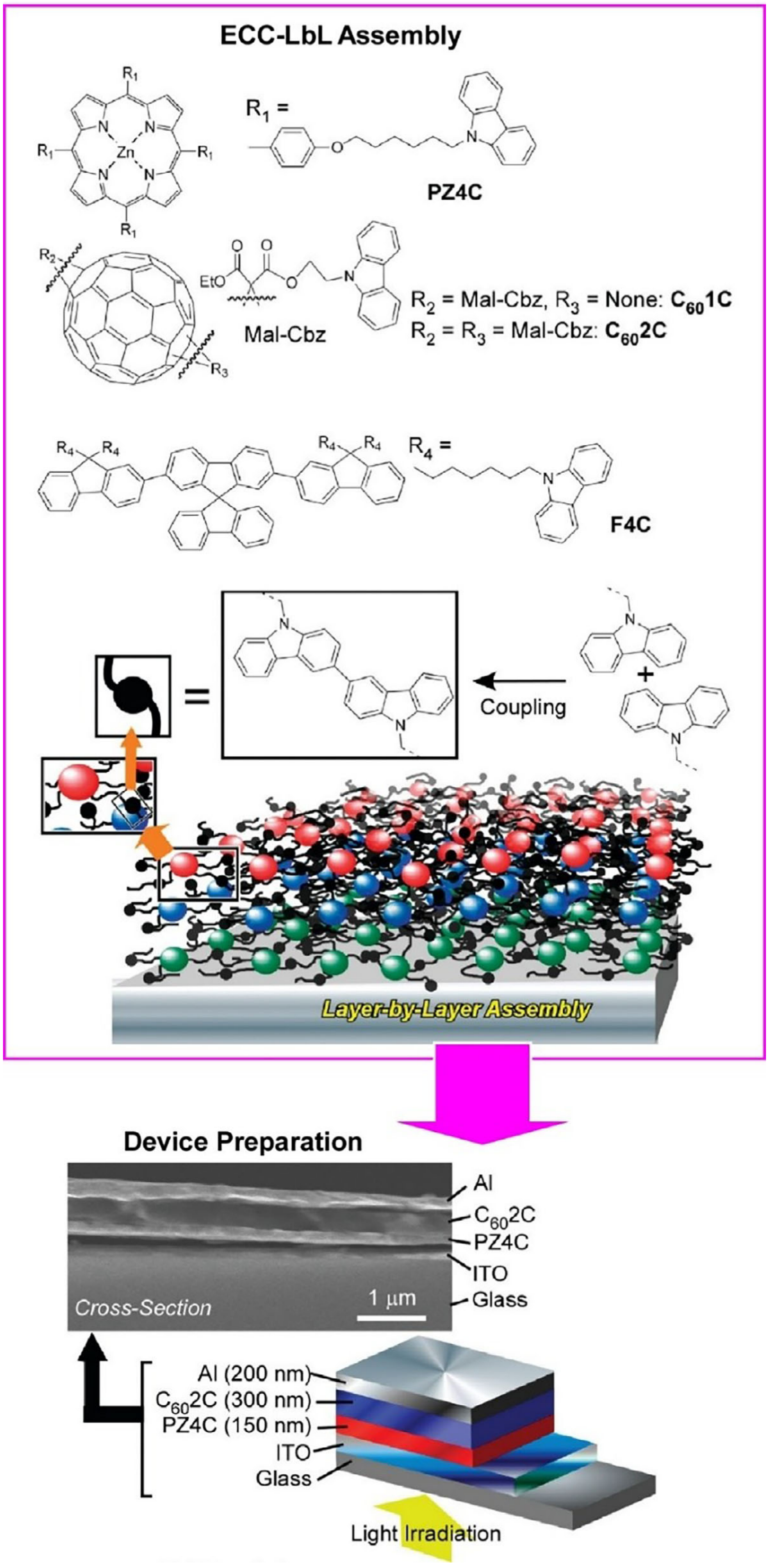

Figure 15. Electrochemical coupling LbL (ECC-LbL) assembly, in which molecular thin films are sequentially immobilized on electrodes by electrochemical coupling reactions, dimerization of *N*-alkylcarbazole, in this case: (top) components for ECC-LbL assembly; (bottom) device preparation. Reproduced with permission.[43] Copyright 2011, American Chemical Society.

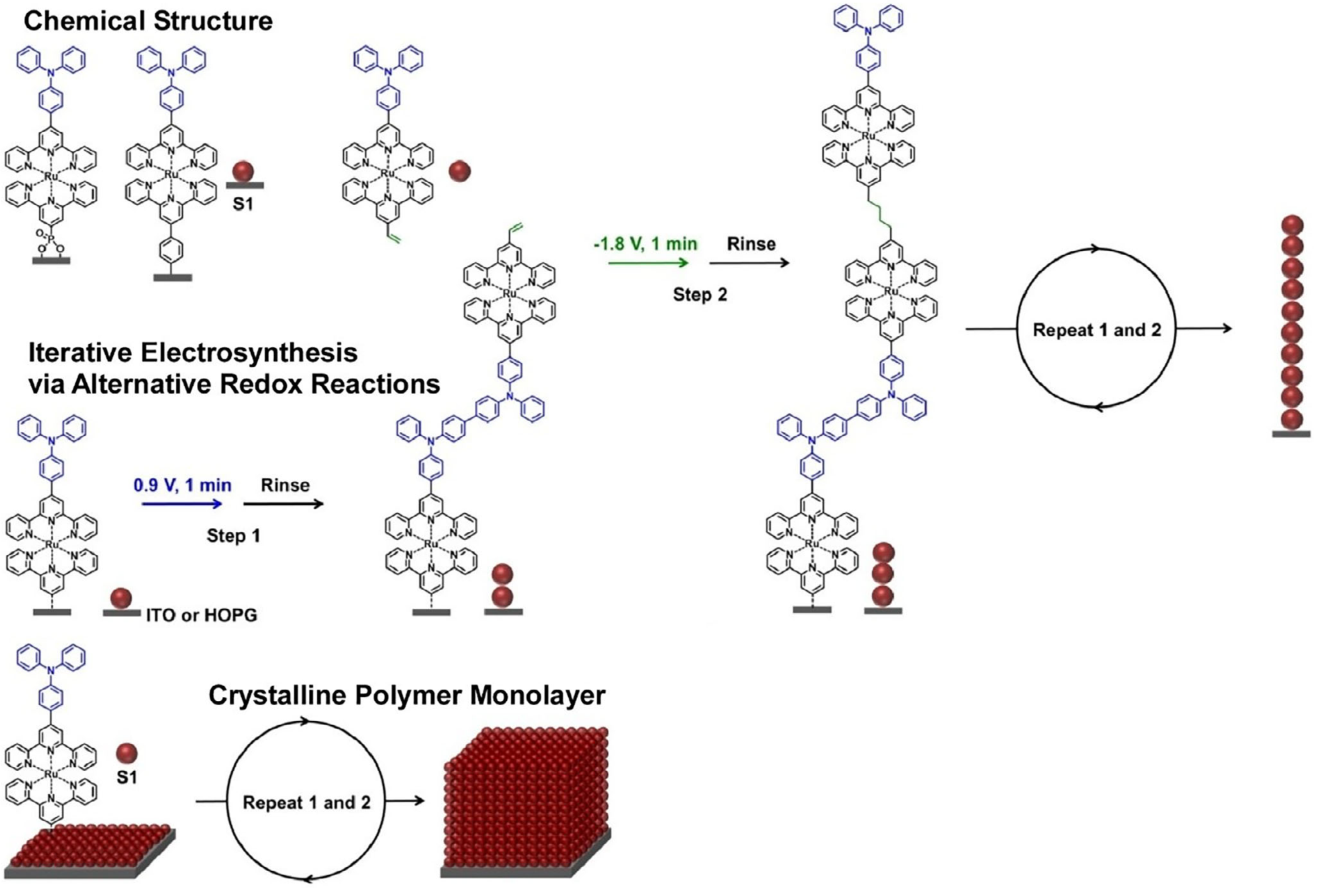

Figure 16. A method to obtain crystalline polymers with well-defined thickness and molecular length by an electrochemical iterative approach, in which starting from a self-assembled monolayer and repeating monomer reaction, the theoretically densest crystalline polymer monolayer is synthesized by solid-phase iterative electrosynthesis. Reproduced with permission.[44] Copyright 2022, Wiley-VCH.

oligomerization, hybrid structures (components, sequences, and shapes) are exemplified in this section. Next, as popular targets, on-surface syntheses for graphene nanoribbons are introduced. Finally, different approach based on electrochemical controls on polymerization is explained.

Polymers are molecules that spontaneously polymerize into chains in response to an appropriate trigger. This can be combined with nanotechnology. As a pioneering example, Okawa and Aono reported that they could use the probe tip of a scanning tunneling microscope (STM) to initiate and terminate the linear propagation of a polymerization reaction at any point in a self-assembled film of diacetylene-type molecules with a spatial precision of about 1 nm (**Figure 18**).[46] They were able to induce chain polymerization over a small distance. Fine control over nanoscale conductive polymer synthesis and polymer interconnection can create a new paradigm for molecular nanoelectronics that could go beyond silicon-based device technology. They foresaw that it would not only open up the possibility of fabricating new molecular nanoelectronics devices, but also enable several new types of physics and chemistry at the nanoscale to be experimentally demonstrated. Measurement of electrical conduction in structurally perfect one-dimensional materials and analysis of the mechanism of chain polymerization propagation could be demonstrated at the molecular level.

On-surface synthesis has enabled the observable synthesis of a wide variety of functional polymers. For example, the bicyclo[1.1.1]pentane motif is important as an sp^3-rich bioisostere of the benzene ring and as a molecular building block in materials science. Yang et al. successfully synthesized polyphenylene wires regularly substituted with rigid aliphatic bicyclopentane insulators by on-surface synthesis (**Figure 19**).[47] The resulting polymers were characterized with submolecular precision. In this work, the behavior of 1,3-disubstituted bicyclo[1.1.1]pentane moieties on metal surfaces is investigated by combining low-temperature STM/non-contact atomic force microscopy (AFM) studies and density functional theory (DFT) modeling. Individual bicyclo[1.1.1]pentane-containing precursors on Au(111), their supramolecular assemblies and thermally activated dehalogenation-coupling reactions leading to polymer chains containing electronically isolated units are directly observed and studied. Thermal treatment of the samples above room temperature triggers dehalogenation and subsequent coupling reactions between the monomers. The result is polyphenylene chains with regularly arranged bicyclo[1.1.1]pentane backbones, which are useful as versatile resistor/insulator units

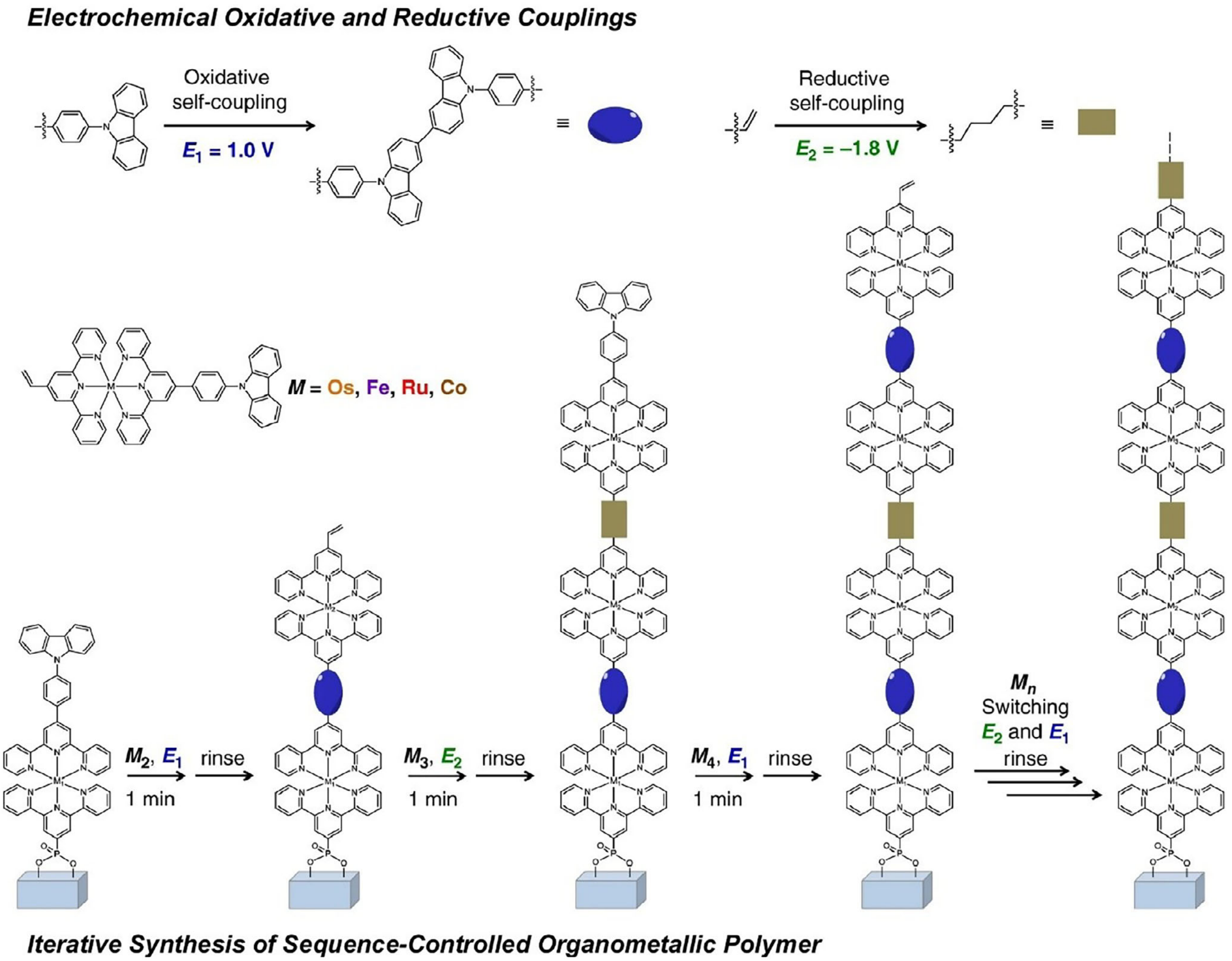

Figure 17. Sequence-controlled electrosynthesis of organometallic polymers with different monomers through oxidative self-coupling of *N*-phenylcarbazolyl and reductive self-coupling of vinyl on pyridine coordinated to the metal core between two monomers. Reproduced under terms of the CC-BY license.[45] Copyright 2020, J. Zhang, J. Wang, C. Wei, Y. Wang, G. Xie, Y, Li, M. Li, Published by Springer-Nature.

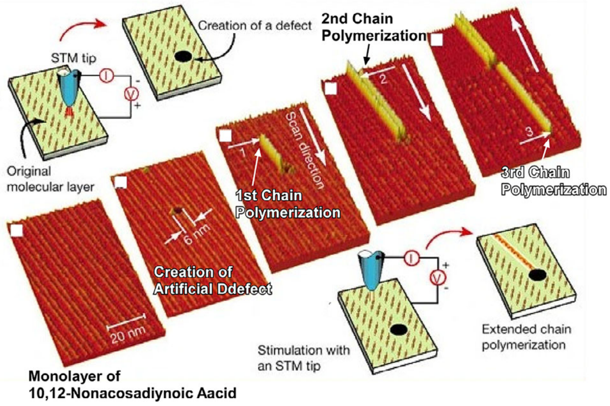

Figure 18. Probe tip activation of a scanning tunneling microscope to initiate and terminate the linear propagation of a polymerization reaction at any point in a self-assembled film of diacetylene-type molecules with a spatial precision of about 1 nm. Reproduced with permission.[46] Copyright 2021, Springer-Nature.

in molecular nanostructures on surfaces. The incorporation of tetrapyrroles and other functional units opens up new avenues for exploring further aspects and tunability of organic electronics.

Not only chain-like polymers, but also ring-linked molecules are of interest. Controlled cyclocarbons, for example, have recently attracted much attention due to their poorly understood geometric and electronic structures in the condensed phase. Xu and co-workers carried out an on-surface synthesis focusing on two antiaromatic cyclocarbons, C_{12} and C_{20} (**Figure 20**).[48] By further extending the surface retro-Bergmann ring-opening reaction by designing two fully halogenated molecular precursors containing four rings, they were able to produce the antiaromatic cyclocarbons C_{12} and C_{20}. The polycyclic structures of C_{12} and C_{20} were revealed by bond-resolved AFM imaging, which was consistent with theoretical predictions. The triple bond assignment was also supported by AFM simulations. DFT calculations of C_{20} on a NaCl surface at different positions showed an almost planar adsorption configuration. The electronic structure of C_{20} can

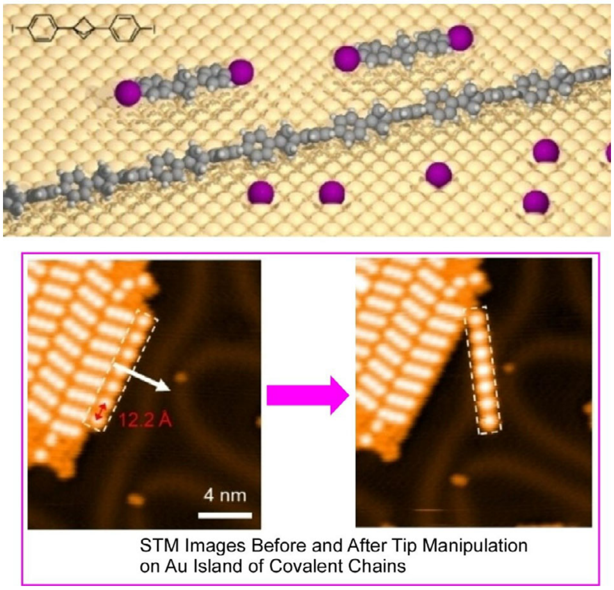

Figure 19. On-surface synthesis of polyphenylene wires regularly substituted with rigid aliphatic bicyclopentane insulators by on-surface synthesis in which supramolecular assemblies of bicyclo[1.1.1]pentane-containing precursors on Au(111) thermally activated dehalogenation-coupling reactions leading to polymer chains containing electronically isolated units. Reproduced under terms of the CC-BY license.[47] Copyright 2023, B. Yang, K. Niu, N. Cao, N. Grover, W. Zhao, A. Riss, J. Björk, W. Auwärter, J. V. Barth, M. O. Senge, Published by Wiley-VCH.

be probed by hindering the diffusion of C_{20}. By delicately positioning the C_{20} molecule within the atomic fence formed by Cl clusters, its boundary molecular orbitals could be probed experimentally.

π-conjugated molecules are considered to be fundamental building blocks for future molecular nanoelectronics. The construction of such block co-oligomers on surfaces has attracted much attention. Kawai and co-workers reported the synthesis of [18]-polyene linked Zn-porphyrin co-oligomers by a two-step reaction of alkyl groups on Cu(111) and Cu(110) (**Figure 21**).[49] The nonyl group ($–C_9H_{19}$), an alkyl group substituted at the 5,15 meso positions of Zn-porphyrin, was first converted to an alkenyl group ($–C_9H_{10}$) by dehydrogenation. Subsequent homocoupling of the terminal -CH_2 groups resulted in extended [18]-polyene-bridged Zn-porphyrin oligomers. In this way, co-oligomers with well-defined alternating unit structures can be generated. This on-surface synthesis methodology may provide a good guideline for the design of more complex macromolecules and functional nanostructures.

The subtle interactions between molecules and the underlying substrate can change the molecular chemisorption direction, which affects the reaction selectivity of the on-surface synthesis process. Zhang, Kim, Xu and co-workers demonstrated that the molecular chemisorption direction can control the reaction selectivity on Au(111) by combining STM images and DFT calculations (**Figure 22**).[50] Specifically, the effect of the molecular chemisorption direction on the reaction selectivity of two types of dehalogenation coupling, polymerization and cyclization, was investigated at the atomic level. When the precursor adsorbed Au(111) substrate was further annealed at 300 K for 10 h, a less ordered covalent structure was formed on Au(111) by intermolecular coupling reactions. Among them, the polymerized oligomers, mainly composed of 4–6 molecular units, had their characteristic alternating morphology as shown by submolecularly resolved STM images. This suggests that the C=C double bonds were formed at the junctions and the molecular units were in a trans-configuration. The reaction selectivity between polymerization and cyclization is strongly influenced by both the radical diffusion and binding barriers at the two chemisorption directions (i.e., 0° and 30°) and the total energy of the stepwise products. This energy barrier varies strongly with the chemisorption direction. In particular, the influence of unfavorable chemisorption directions and conditions on the reaction pathways and products should be re-evaluated, aiming to provide fundamental insights into the tuning of reaction selectivity by exploiting some subtle interfacial parameters in surface reactions.

Ren et al. reported the synthesis of *N*-heterocyclic carbene polymers on gold surfaces consisting of ball-and-socket repeating units attached to Au adatoms (**Figure 23**).[51] A delicate balance between mobility and polymerization rate controls the directionality of the polymer. These polymers are expected to be useful in nanoelectronics, surface functionalization, and catalysis. Long chains are also formed, but the orientation of the polymer can be controlled by the mobility and reactivity of the precursors. This detailed knowledge is expected to be useful for the fabrication of other novel robust carbene-based supramolecular architectures and nanomaterials, as well as for the construction of *N*-heterocyclic carbene-based catalytic surfaces.

The creation of graphene nanoribbons is an important goal for on-surface synthesis. The fabrication of graphene nanoribbons by surface synthesis, combining reactive precursor molecules to form extended polymer structures, offers an approach to increase the structural diversity. Tuning the properties/composition of the precursor molecules results in quasi-1D graphitic wires that can be doped. Combining the atomic precision of solution-phase synthetic chemistry with surface protocols may enable reactions that are not yet possible in solution. Saywell and co-workers have created porphyrin-fused graphene nanoribbons by incorporating porphyrin species into the graphene nanoribbons (**Figure 24**).[52] These take the form of sections of aryl rings that fuse together during the reaction to form graphitic regions between adjacent Ni-porphyrin units. Porphyrin-fused graphene nanoribbons are synthesized on surfaces as linear polymers consisting of regularly spaced Ni-porphyrin units. A periodic sequence of bright features is intercrossed along the chains. This is due to alternating regions of polycyclic aromatic hydrocarbons and porphyrin sections in the polymer chains. This indicates that Ni-porphyrin units are incorporated into the nanoribbons. By combining atomically precise solution-based synthesis and surface reaction routes, the formation of graphene nanoribbons doped with functional units such as porphyrin has been demonstrated. The surface synthesis of such functional molecular structures offers a route to the development of materials with tailored catalytic, optoelectronic and magnetic properties.

Campañ, de la Torre, and co-workers demonstrated the preparation of low bandgap fulvalene-bridged bisanthene polymers (**Figure 25**).[53] They used 9,10-bis(trimethylsilyl)ethynylanthracene and 10,10′-

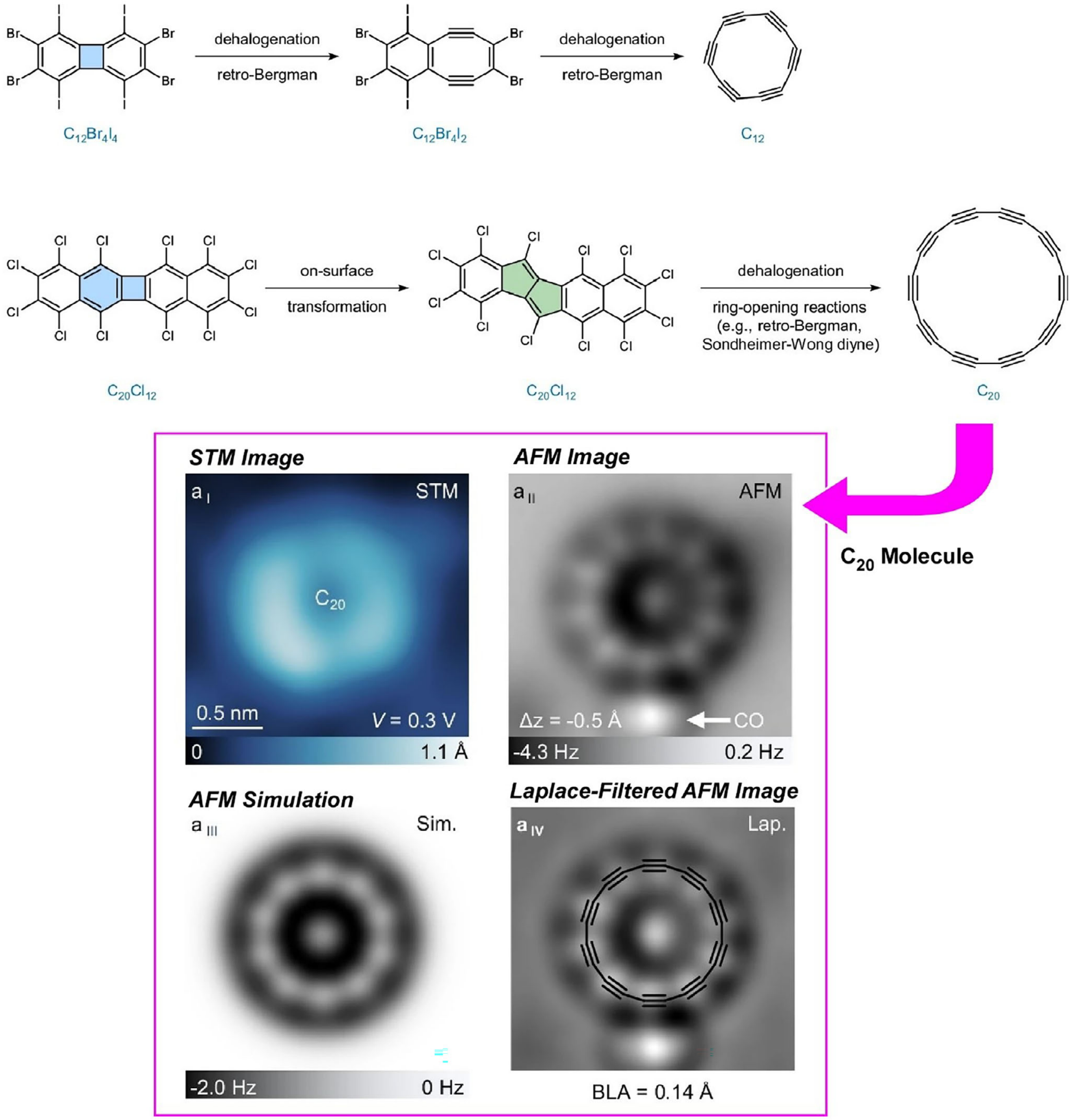

Figure 20. On-surface synthesis focusing on two antiaromatic cyclocarbons, C_{12} and C_{20}: synthetic scheme (top) and images (bottom). Reproduced with permission.[48] Copyright 2024, Springer-Nature.

bis((trimethylsilyl)ethynyl)-9,9′-bianthracene as precursors. They exploited the atomic rearrangement of ethynylarenes into cyclopenta-condensed polycyclic aromatic hydrocarbons to prepare low bandgap fulvalene-bridged bisanthene polymers on the atomically flat Au(111) surface. The fulvalene-bridged bisanthene polymers exhibited an experimentally narrow electronic frontier gap of 1.2 eV on Au(111) with fully conjugated units. This on-surface synthesis strategy can be extended to other conjugated polymers, and their optoelectronic properties can potentially be tuned by incorporating five-membered rings at precise positions. The new synthetic strategy paves the way for the preparation of highly functional covalent polymers, which are particularly attractive for organic photovoltaics, photodetectors and ambipolar field-effect transistors.

The on-surface synthesis of edge-functionalized graphene nanoribbons has attracted considerable attention. However, it is

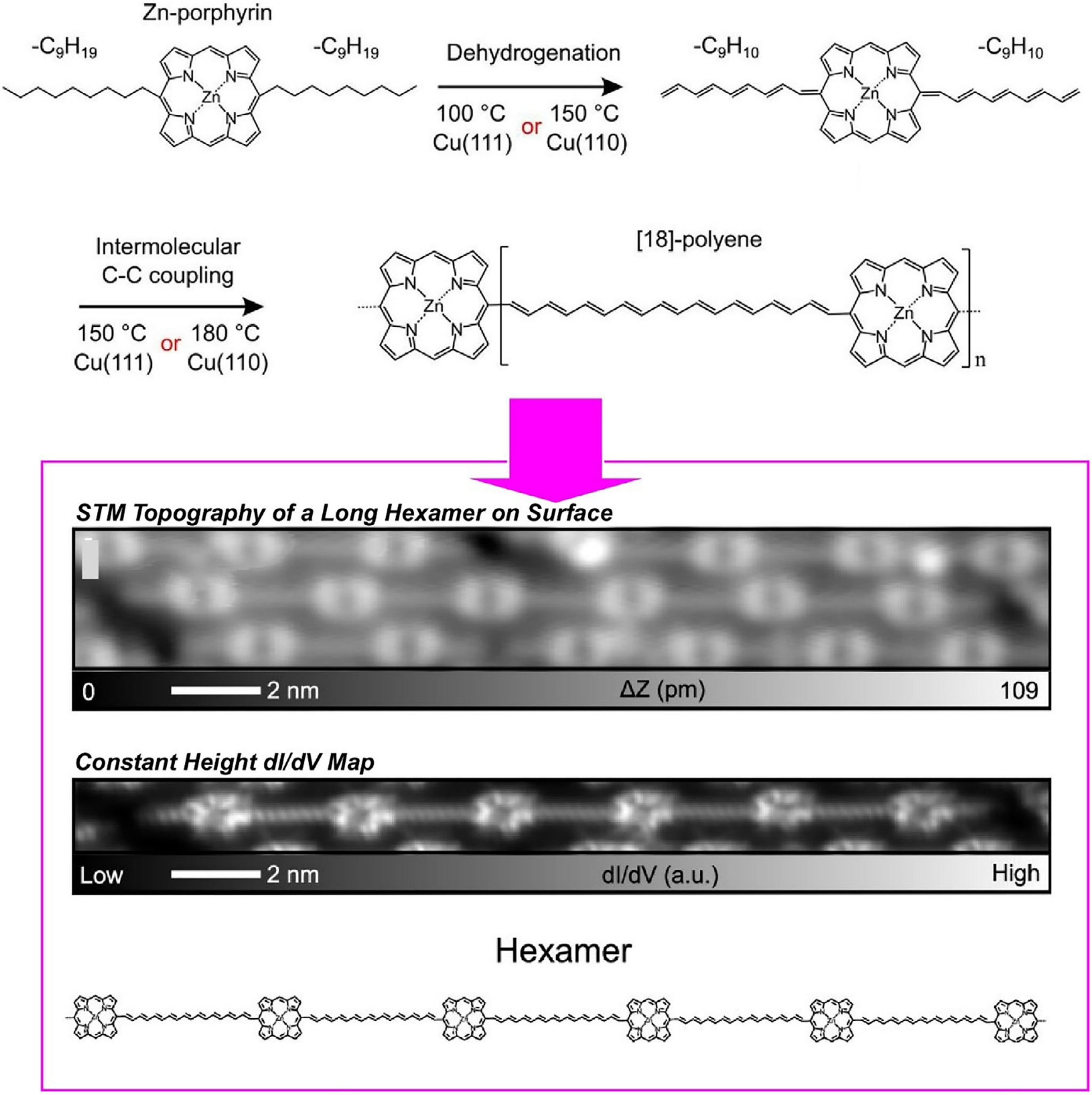

Figure 21. On-surface synthesis of[18]-polyene linked Zn-porphyrin co-oligomers by a two-step reaction of alkyl groups on Cu(111) and Cu(110): synthetic scheme (top) and images of hexamer (bottom). Reproduced with permission.[49] Copyright 2024, American Chemical Society.

difficult to produce graphene nanoribbons on a large scale by surface synthesis under ultra-high vacuum on thermally activated metal surfaces. This is due to the decomposition of functional groups at temperatures of 300–500 °C and the limited growth of single-layer graphene nanoribbons based on metal catalysts. To overcome these obstacles, Sakaguchi et al. developed a surface electrochemistry technique that exploits the redox reaction of asymmetric precursors in an electric double layer where a strong electric field is confined to the liquid–solid interface (**Figure 26**).[54] This technique utilizes redox reactions such as ionic polymerization and oxidative dehydrogenation that occur in the electric double layer at the liquid–solid interface. The use of an electric double layer allows the confinement of a strong electric field to a thickness of about 1 nm at the solid–liquid interface. This confinement enables the generation of active intermediates that promote the multilayer growth of graphene nanoribbons through redox reactions at very low temperatures. This study demonstrates the heterochiral growth of armchair-edge graphene nanoribbons with covalently bound butoxy substituents on an electrode surface from an electrolyte

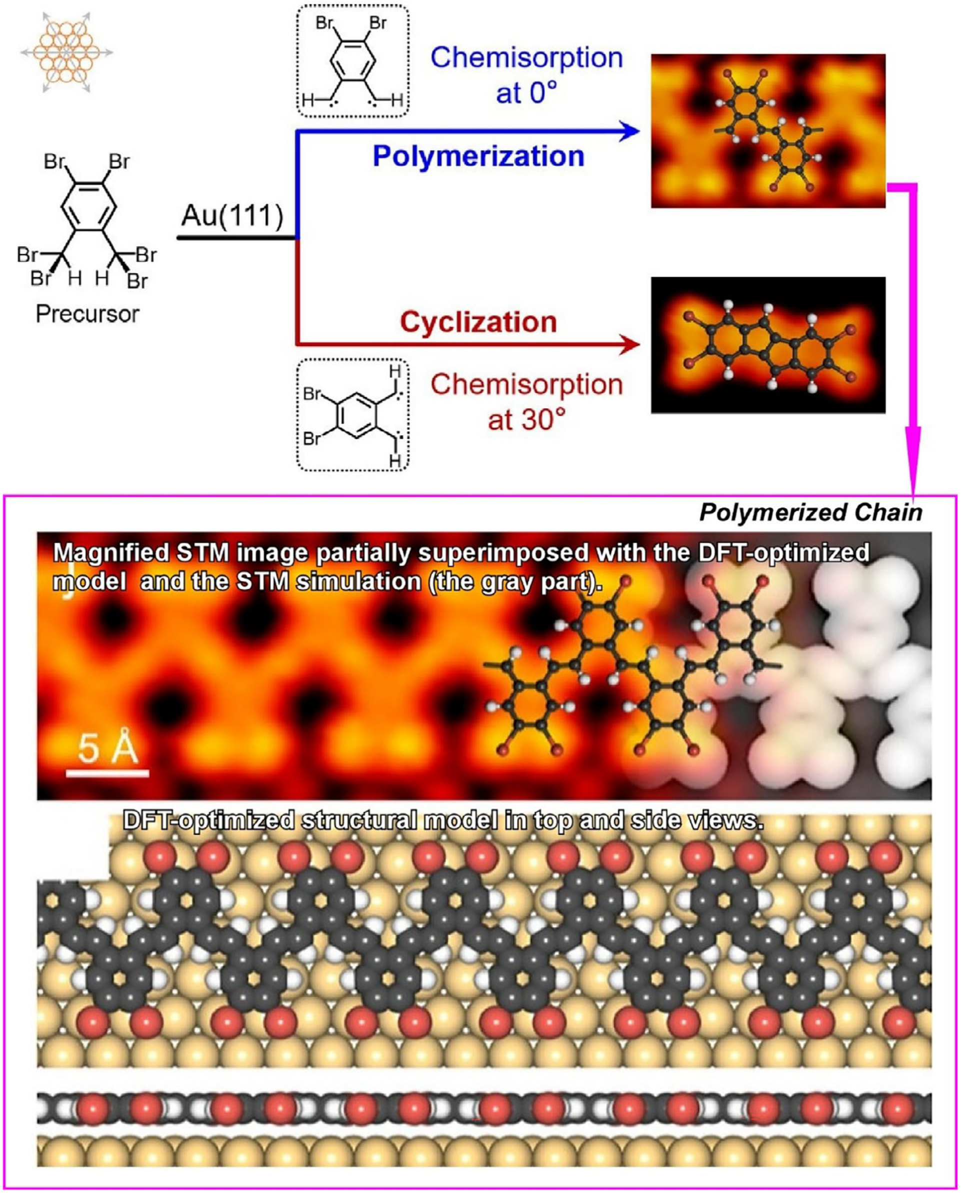

Figure 22. Effect of the molecular chemisorption direction on the reaction selectivity of two types of dehalogenation coupling, polymerization and cyclization on Au(111) investigated by combining STM images and DFT calculations. Reproduced with permission.[50] Copyright 2024, American Chemical Society.

solution containing 2-butoxynaphthalene. Strongly electron-donating graphene nanoribbons has been successfully grown LbL on an electrode at temperatures below 80 °C without decomposing the functional groups. High voltages were shown to promote previously unknown heterochiral dicationic polymerization. Furthermore, the electrochemically prepared graphene nanoribbons exhibited superior silicon etching properties compared to noble metals. They also showed excellent photoconductivity. This electrochemical surface synthesis can be applied to a variety of aromatic precursors; therefore, it can lead to a wider range of graphene nanoribbons. It also has great potential for application in Si nanolithography.

This section has shown examples of on-surface synthesis of polymers and related molecules on solid surfaces. Chemical reactions and their products can be observed as molecular images. The presented examples clearly indicate advantages of direct observations for surface reactions of polymerization and oligomerization. Not limited to exploration of new techniques, these approaches will figure out fundamentals on polymer science. For example, chemical reactions on surfaces are governed by the mutual orientation of the molecules and their interactions with the substrate surface. Reaction selectivity can be observed that is different from that in solution, and reactions that are difficult to observe in solution can occur at interfaces. Polymer synthesis can take place not only in dry vacuum environments, but also by applying high voltage in electrical double layers. On-surface synthesis is a strong fusion of traditional materials chemistry, such as organic synthesis and polymer synthesis, and

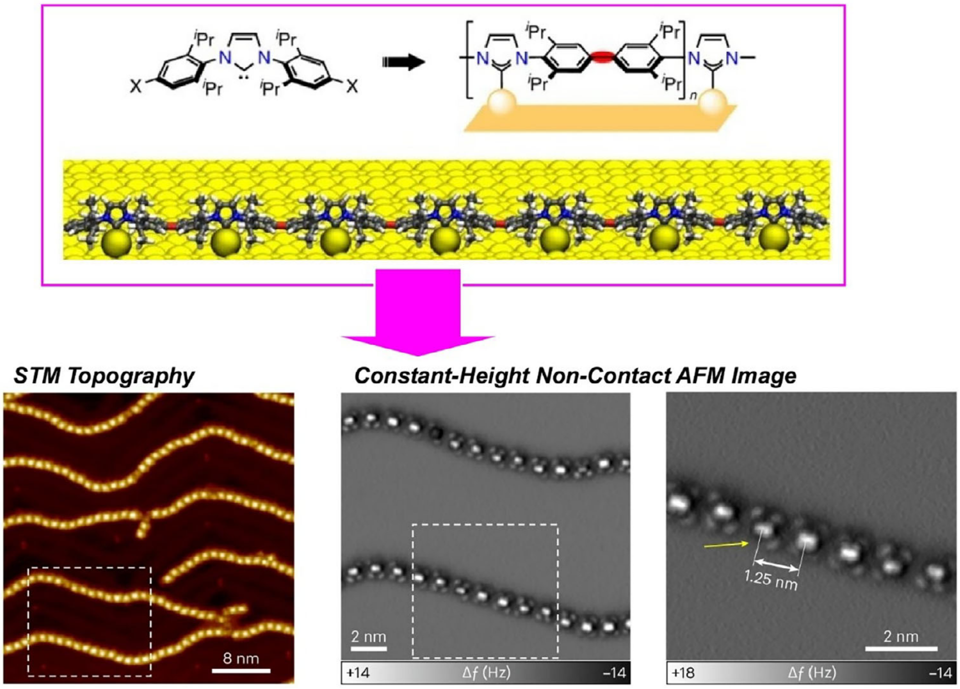

Figure 23. Synthesis of *N*-heterocyclic carbene polymers on gold surfaces consisting of ball-and-socket repeating units attached to Au adatoms. Reproduced with permission.[51] Copyright 2023, Springer-Nature.

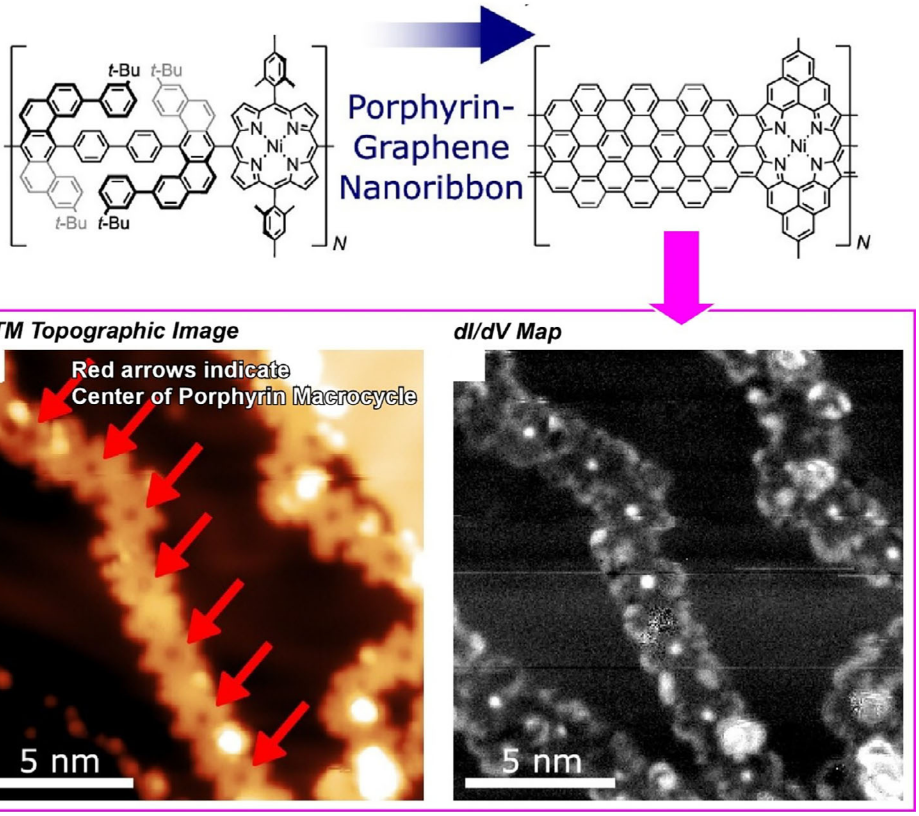

Figure 24. Synthesis of porphyrin-fused graphene nanoribbons by incorporating porphyrin species into the graphene nanoribbons as linear polymers consisting of regularly spaced Ni-porphyrin units. Reproduced under terms of the CC-BY license.[52] Copyright 2024, M. Edmondson, M. Clarke, J. N. O'Shea, Q. Chen, H. L. Anderson, A. Saywell, Published by American Chemical Society.

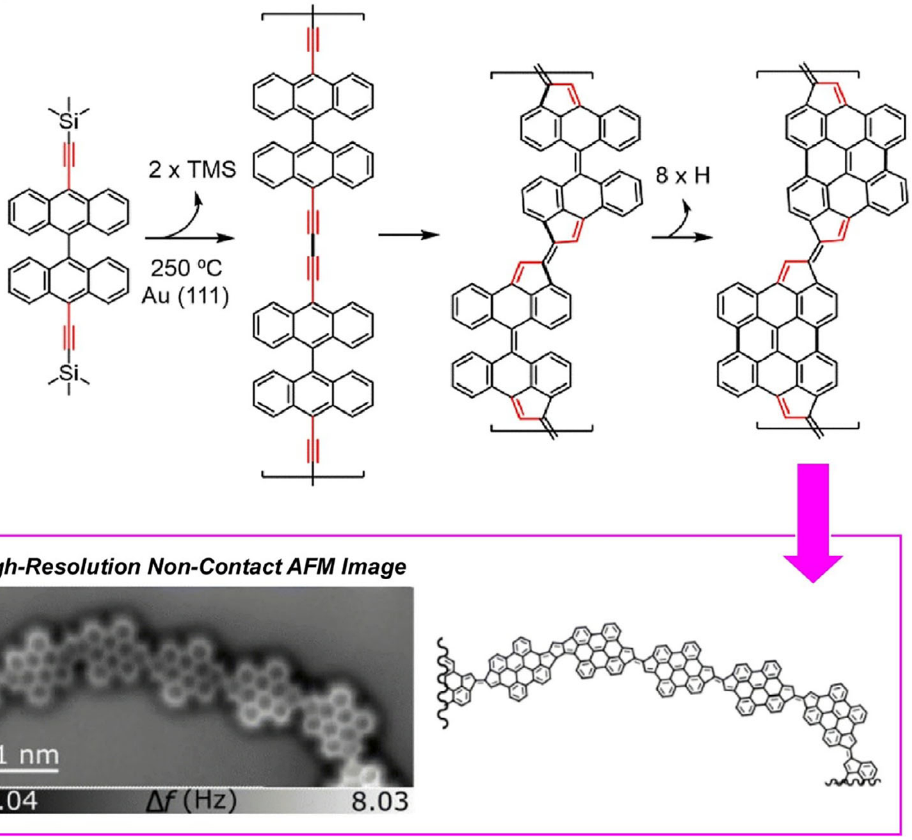

Figure 25. Synthesis of low bandgap fulvalene-bridged bisanthene polymers using 9,10-bis(trimethylsilyl)ethynylanthracene and 10,10′-bis((trimethylsilyl)ethynyl)-9,9′-bianthracene as precursors. Reproduced under terms of the CC-BY license.[53] Copyright 2023, A. Jiménez-Martín, F. Villalobos, B. Mallada, S. Edalatmanesh, A. Matěj, J. M. Cuerva, P. Jelínek, A. G. Campaña, B. de la Torre, Published by Royal Society of Chemistry.

nanotechnology. It can be seen as a simple embodiment of nanoarchitectonics. We have to note a wider possibilities on surface synthesis of functional polymers. Not limited to on-surface synthesis with microscopic observation, electrochemical surface synthesis of polymers has been researched. For example, electroclick reactions at surfaces can give polymers and hybrid films conjugated with nanoparticles and capsules.[55] Advanced structures of polymers with transition metal coordination[56] and gradient surfaces[57] can be prepared through electrochemical surface synthesis.

5. Other Approach

The previous three sections have introduced polymer nanoarchitectonics using typical interfacial techniques such as the LB method, LbL assembly, on-surface synthesis, etc. This section will present examples of interfacial processes that are not typical of polymer synthesis, but can provide inspiration for polymer nanoarchitectonics. In the first examples, polymerization of fullerenes and their materializations are discussed. As effects of these examples, 2D materials like carbon material preparations and internal carbon framework control are exemplified as frontier of precise nanostructure controls in materials level. The last example shows supramolecular interfacial doping of polymeric semiconductor films as an emerging approach for manipulation of functional polymer films.

A method has also been reported to synthesize graphene-like 2D carbon materials by assembling fullerene C_{60} molecules as a molecular film at a liquid interface, linking them and treating them at high temperatures. Song et al. reported the bottom-up preparation of a new molecularly thin 2D nanocarbon material called "fullerphene," which can be doped with nitrogen (**Figure 27**).[58] The coexistence of fullerene C_{60} and ethylenediamine produces an ethylenediamine adduct of C_{60}, which has both hydrophilic and hydrophobic properties and is surface active. This C_{60} compound self-assembles and cross-links at the liquid–liquid interface (water–mesitylene interface) to form a large area molecularly thin 2D fullerene-ethylenediamine polymer film. A subsequent carbonization process at 700 °C synthesizes a carbon nanofilm. The reconstructed ultrathin 2D structure is graphene-like and is called fullerphene because it is synthesized from fullerene. The resulting structure retains the nanofilm morphology even after the carbonization process. Fullerphene is a nitrogen-doped ultrathin carbon film. It also has a structure that contains both hierarchical micropores and mesopores on its surface. These structural properties allow selective and repeated adsorption and desorption of low molecular weight carboxylic acid vapors through non-covalent interactions. Carboxylic acids can be discriminated at the single carbon atom level, such as the sharp

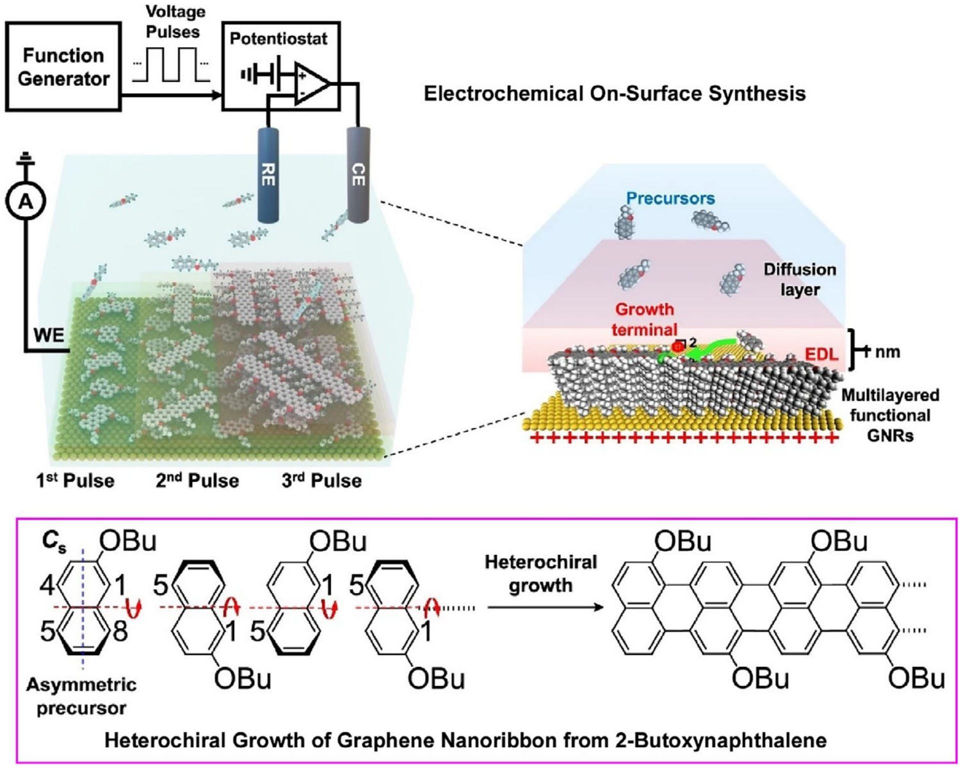

Figure 26. Surface electrochemistry technique to promote the multilayer growth of graphene nanoribbons through redox reactions at very low temperatures as grown layer-by-layer on an electrode at temperatures below 80 °C without decomposing the functional groups. Reproduced under terms of the CC-BY license.[54] Copyright 2024, H. Sakaguchi, T. Kojima, Y. Cheng, S. Nobusue, K. Fukami, Published by Springer-Nature.

distinction between formic acid and acetic acid. This method may be applicable to other substrates. The liquid–liquid interface environment could be used as a method to develop new 2D materials through molecular modification, polymerization and heat treatment.

The method of fabricating nanocarbon materials from the fullerene C_{60} can lead to control of the atomic framework of carbon materials. Chen et al. assembled C_{60} molecules using ethylenediamine at the interface of a NaCl template, converted them into carbon materials by high temperature treatment, and investigated their catalytic activity for the oxygen reduction reaction (**Figure** 28).[59] The morphology and size of the cavities in the cage structure were similar to those of the template NaCl nanocrystals. High-resolution TEM images of selected areas showed that the carbon walls of the cages were about 10–14 nm thick and were essentially amorphous carbon structures. When nitrogen-doped cage-like carbon was annealed at 800–1100 °C in a nitrogen atmosphere, the doped pyridine nitrogen atoms were removed. The removal of the nitrogen atoms resulted in the formation of pentagons. This strategy succeeded in deliberately creating a nanoarchitectonics of pentagonal atomic frameworks in nanocarbon materials. This structure increases the catalytic activity for the oxygen reduction reaction. Catalysts with a high concentration of pentagonal frameworks exhibit higher magnetism, which is thought to induce singly occupied molecular orbitals and contribute to improved performance. DFT calculations support the role of spin in enabling O_2 adsorption to enhance activity. Interfacial nanoarchitectonics, which can even control the atomic framework in nanocarbons, could be a new principle for catalyst design, highlighting the importance of pentagons with electronic spin in the design of carbon-based catalysts.

The control of organic semiconductor functions at interfaces is also being investigated. Chemical doping of molecular semiconductors is based on electron transfer reactions between semiconductor and dopant molecules. A method has also been reported in which doping structures are nanoarchitecturized by coupling with chemical reactions at the interface of polymer-semiconductor thin films. Ishii, Yamashita, and co-workers developed a chemical doping technique for polymer semiconductors using the redox reaction of benzoquinone and hydroquinone in ambient aqueous solution (**Figure** 29).[60] Proton-coupled electron transfer is a mechanism used in the electron transport system of photosynthesis, among other things. When a polymer semiconductor thin film was immersed in an aqueous solution of benzoquinone, hydroquinone and hydrophobic anions, p-type doping was confirmed. Although proton-coupled electron transfer does not generate ionic species that act as dopant ions, it was found that efficient chemical doping of polymer semiconductors can be achieved by a synergistic action between proton-coupled electron transfer and insertion of hydrophobic ions. According to the Nernst equation, the doping level changes with the pH of the aqueous solution, and the electrical conductivity was precisely and consistently controlled over a wide range of about five orders of magnitude. This method shows unprecedented scalability, stability and tunability compared to conventional chemical

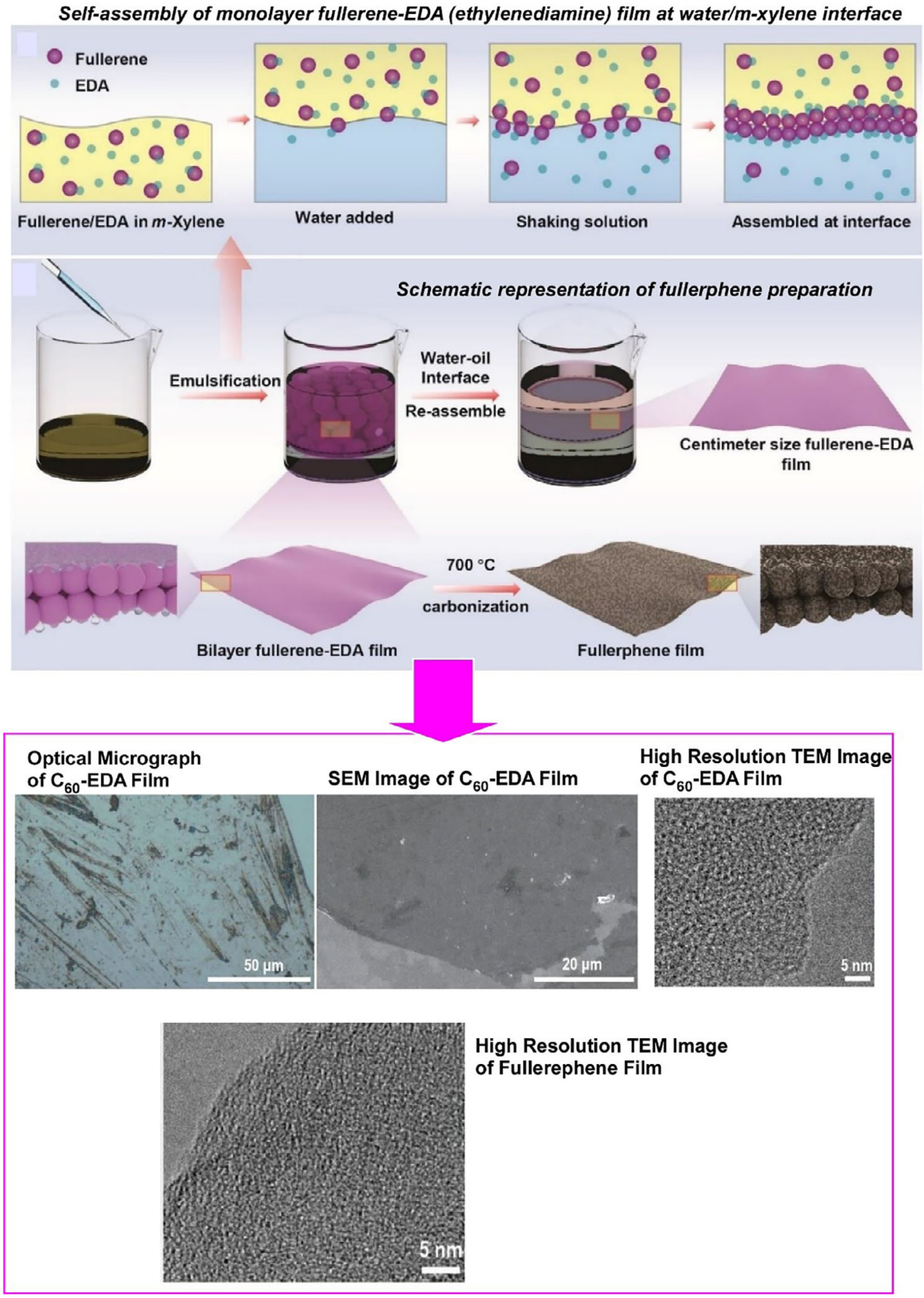

Figure 27. Bottom-up preparation of a molecularly thin 2D nanocarbon material called "fullerphene" doped with nitrogen: synthetic procedure (top) and images (bottom). Reproduced with permission.[58] Copyright 2022, Wiley-VCH.

doping methods carried out in organic solvents under vacuum or inert atmosphere. The relationship between semiconductor doping and proton activity may be useful in creating a platform for room temperature semiconductor processes and biomolecular electronics. Polymer semiconductors are flexible, lightweight and suitable for low-cost printing processes such as inkjet printing. This technology is expected to drive industrial applications of flexible devices such as film-type sensors, electronic circuits, displays, and solar cells. Film-type pH sensors using this technology are also expected to be used in healthcare and biosensing applications.

This section presents some pioneering examples of nanoarchitectonics of polymers at interfaces and derived materials. These examples break with the conventional wisdom of functional materials development, including bottom-up synthesis of novel 2D materials, control of nanocarbon structure down to the atomic skeleton, and precise doping of polymer-semiconductor thin films in aqueous systems under ambient conditions. In each

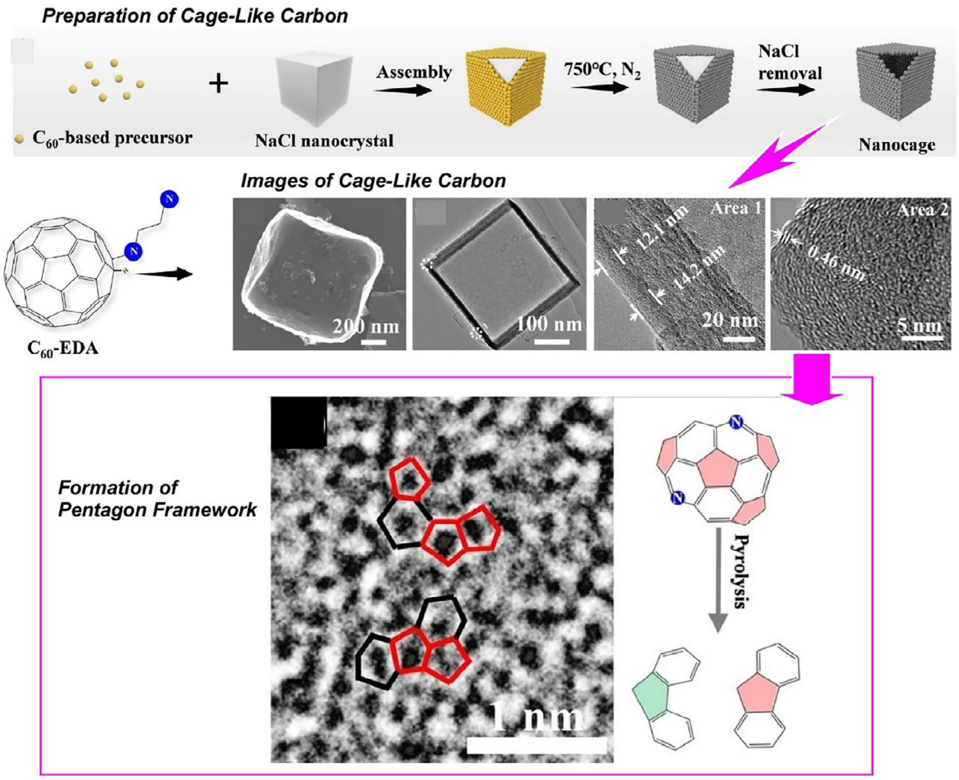

Figure 28. Preparation of carbon nanocage through assembly of C_{60} molecules using ethylenediamine at the interface of a NaCl template, followed by conversion of them into carbon materials by high temperature treatment (top), resulting in the formation of pentagon carbon frameworks (bottom). Reproduced under terms of the CC-BY license.[59] Copyright 2024, G. Chen, M. Isegawa, T. Koide, Y. Yoshida, K. Harano, K. Hayashida, S. Fujita, K. Takeyasu, K. Ariga, J. Nakamura, Published by Wiley-VCH.

example, the nanoarchitectonics concept is at work, coupling material accumulation, carbonization and interfacial reactions. The examples indicate that wise combinations of existing techniques can lead to very precise controls of structure and properties of polymeric substances and related materials. This confirms the unexplored potentials of interfacial nanoarchitectonics in polymer science and technology. In addition, we have to note that further potential possibilities on polymer nanoarchitectonics would be found in well-known examples. For example, block copolymers are also suitable nano-units for nanoarchitectonics on surfaces because of their propensity to form well-defined microphases. Such films are usually assembled by dip/spin coating. Several nice research examples are continuously reported.[61]

6. Summary and Perspectives

This review, entitled "Nanoarchitectonics of Polymers at Interfaces," discusses the research trends in the construction of functional polymer materials, focusing on nanoarchitectonics, and interface technology. In particular, this review focuses on the LB method, LbL assembly and on-surface synthesis, and give typical examples to explore the trends. Langmuir monolayers at the air–water interface and LB films provide a forum for elucidating fundamental properties such as the orientation of polymer chains and the photoelectron functions based on them. Because of the aqueous environment and the high degree of designability of ultrathin films at the molecular level, they are very useful as models and mimics of biological membranes. There are high expectations for their development in medical applications related to cell membranes. In LbL assembly, in addition to the conventional layering process by electrostatic interaction, improvements such as interlayer fixation by covalent bonds have been explored. This is useful for applications where sufficient mechanical strength is required. It can be further developed to create a methodology for the stepwise formation of covalent bonded polymers from the surface, which may lead to a new method of polymer synthesis. On-surface synthesis on solid surfaces can show different reaction selectivity than synthesis in solution, and reactions that are difficult to see in solution can occur. On-surface synthesis has a strong aspect of merging traditional materials chemistry, such as organic synthesis and polymer synthesis, with nanotechnology. This can be seen as a simple embodiment of nanoarchitectonics. Other examples of interfacial nanoarchitectonics research that break the conventional wisdom of functional materials development include bottom-up synthesis of new 2D materials, control of nanocarbon structures down to the atomic skeleton, and precise doping of polymer-semiconductor thin films in aqueous systems.

Even if we focus on typical interface technologies, we can see examples of the development of functional polymer materials with a variety of developments such as those mentioned above. The key to further developments of this technology are the combination of these technologies and their response to industrialization. Polymer design and synthesis is diverse and can be designed

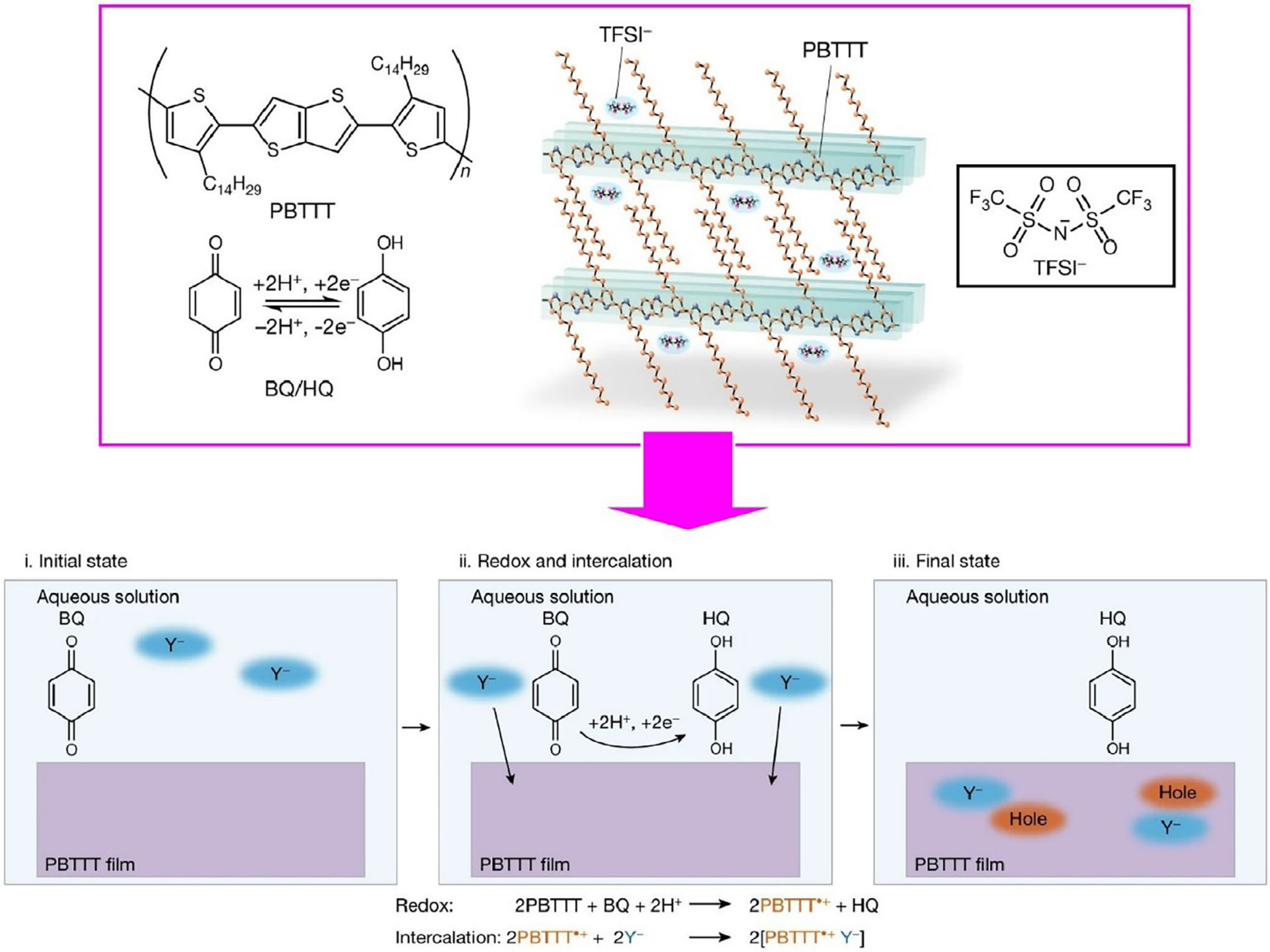

Figure 29. A chemical doping technique for polymer semiconductors using the redox reaction of benzoquinone and hydroquinone in ambient aqueous solution. Reproduced with permission.[60] Copyright 2023, Springer-Nature.

to perform a variety of functions. At present, development is being carried out to specialize in one particular function in most the cases. In the future, it should be promoted to build multifunctional materials that integrate them from a variety of polymer materials. Therefore, the mission of polymer nanoarchitectonics should be to build a large number of functional polymers into rational structures. Interface technology will be an important tool in this regard. Ideally, functional polymer materials with very versatile functions should be developed. Upon the assembly of the various precursors to give the corresponding polymer nanoarchitectonics, the interaction in-between/among the building blocks plays a key role. These interactions among a large number of functional precursors and polymer units have to be controlled in rational ways. However, this may be difficult to achieve with only the knowledge and experience of researchers and basic theories. It is essential to introduce artificial intelligence that can handle large amounts of data. It is desirable to apply machine learning[62] and materials informatics,[63] which have been introduced in many areas of chemistry, to polymer nanoarchitectonics. The fusion of nanoarchitectonics and materials informatics has also been proposed in other materials developments.[64] A future direction for polymer nanoarchitectonics is to develop multifunctional polymer materials by introducing artificial intelligence technology.

Polymer materials are a typical example of materials that are easy to put to practical use. Another direction is the practical application of the nanostructure-controlled functional polymer materials presented in this paper. To achieve this, it is necessary to go back to the basics of interface technology and consider reforms that will bring innovation to the method. For example, in the case of LbL assembly, a spray method has been developed instead of the conventional dipping method.[65] This development has made it extremely easy to produce LbL films. It has also been proposed to apply this method to car washes to coat the surface of a car with an LbL film.[66] In addition, in the development of high quality polymer semiconductor thin films, it has been shown that the use of a non-aqueous liquid phase makes it possible to produce LbL films at high temperatures with much better annealing effects.[67] The idea of using water at room temperature breaks with conventional wisdom and makes it possible to produce nano-thin films with orientation and stacking suitable for practical use. An LB film preparation apparatus for high temperature LB methods has also been developed.[68] As can be seen from these examples, the application of interface technology to previously unimaginable methods can contribute to polymer nanoarchitectonics that was previously unattainable. Polymer materials are suitable for industrialization, and it can be believed that interface technology should be reformed to take advantage of the advanced functionality of nanoarchitectonics.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

interfaces, Langmuir–Blodgett technique, layer-by-layer assembly, nanoarchitectonics, on-surface synthesis, polymer

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