On-Surface Covalent Synthesis of Carbon Nanomaterials by Harnessing Carbon *gem*-Polyhalides

José I. Urgel, Ana Sánchez-Grande, Diego J. Vicent, Pavel Jelínek, Nazario Martín, and David Écija**

The design of innovative carbon-based nanostructures stands at the forefront of both chemistry and materials science. In this context, π-conjugated compounds are of great interest due to their impact in a variety of fields, including optoelectronics, spintronics, energy storage, sensing and catalysis. Despite extensive research efforts, substantial knowledge gaps persist in the synthesis and characterization of new π-conjugated compounds with potential implications for science and technology. On-surface synthesis has emerged as a powerful discipline to overcome limitations associated with conventional solution chemistry methods, offering advanced tools to characterize the resulting nanomaterials. This review specifically highlights recent achievements in the utilization of molecular precursors incorporating carbon *geminal (gem)*-polyhalides as functional groups to guide the formation of π-conjugated 0D species, as well as 1D, quasi-1D π-conjugated polymers, and 2D nanoarchitectures. By delving into reaction pathways, novel structural designs, and the electronic, magnetic, and topological features of the resulting products, the review provides fundamental insights for a new generation of π-conjugated materials.

1. Introduction

On-surface synthesis has recently emerged as a potent method for designing carbon-based nanomaterials that were previously difficult to produce, efficiently bypassing challenges associated with conventional synthetic methods, particularly those linked to low solubility and high reactivity in solvents. This innovative synthetic paradigm involves depositing molecular precursors onto a pristine surface under ultra-high vacuum conditions and subsequently inducing intra- and intermolecular reactions through the application of external stimuli such as thermal annealing, light irradiation, or electron beams. Following this approach, the on-surface synthesis community has uncovered unprecedented synthetic mechanisms and novel nanomaterials explored by sub-molecular resolution scanning probe microscopy techniques.[1–4]

While modern chemistry traces its roots back to the 18th century, on-surface synthesis is still in its nascent stages, and it is not surprising that only a handful of chemical reactions have been exemplified. Noteworthy, among these reactions[1–3] are dehalogenative homocoupling (including the archifamous Ullmann coupling),[5–14] alkyne homocoupling,[15] direct C-H activation,[16,17] condensation reactions,[18,19] and intramolecular dehydrogenations.[13,20–22]

A pivotal pursuit in this burgeoning on-surface synthesis discipline is the exploration of diverse functional groups to guide distinctive synthetic strategies. Herein, carbon *geminal (gem)*-polyhalides are functional groups in which a carbon atom is functionalized by two or more halogen atoms. While the chemical activity of aryl monohalides on surfaces has been extensively investigated and discussed in previous reviews,[3,6,14] mostly focusing on the well-known Ullmann coupling reaction, a comprehensive overview of carbon *gem*-polyhalides on surfaces is lacking. In this regard, this review first introduces the role of carbon *gem*-polyhalides in molecular precursors or intermediates for further conventional syntheses, describing their most common uses. Then, the versatile capabilities of carbon *gem*-polyhalides are reported for generating π-conjugated 0D products, 1D molecular wires, quasi-1D ladder polymers, and 2D patches on metallic surfaces.

Three different approaches to activate these functional groups and trigger the desired chemical reactions are reviewed. The first and most studied method is the deposition of a precursor on a substrate followed by subsequent annealing steps to afford the desired carbon-based nanomaterials. Notably, non-trivial topology is expressed in some of these polymers, thus anticipating fascinating avenues in the realm of condensed matter physics. Second, by depositing the precursor on a hot substrate targeting to activate previously precluded intramolecular reactions,

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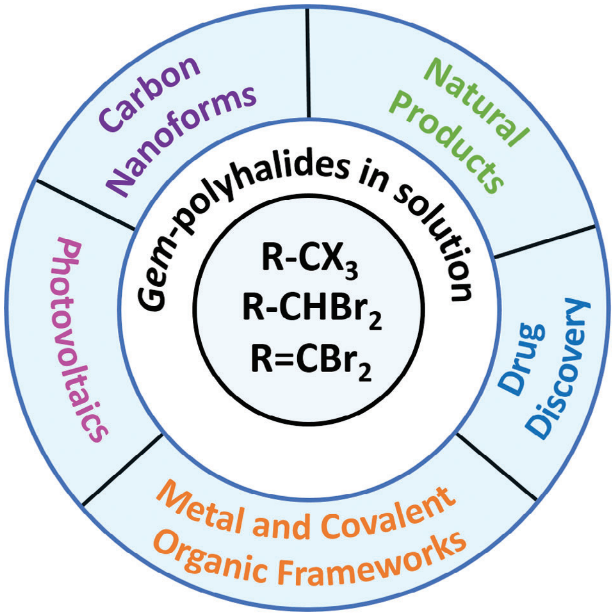

Figure 1. Scheme of the most frequent uses and applications of molecular carbon *gem*-polyhalides functional groups in solution chemistry. X stands for F, Cl or Br.

individual products, organometallic compounds and quasi-1D π-conjugated ladder polymers are obtained. Finally, the use of tip-induced atomic manipulation has allowed to trigger dehalogenation, and, by inducing carbon skeletal rearrangements, afforded the fabrication of exotic carbon allotropes.

In summary, carbon *gem*-polyhalides are revealed as an emerging set of powerful functional groups for tailoring unique carbon-based nanomaterials by on-surface synthesis with potential scientific and technological impact in a variety of topics such as (opto)-electronics, spintronics, quantum information, sensing and catalysis, to name a few, thus complementing and enriching the so far known applications of these less-common functionalities.

2. Carbon *gem*-Polyhalides in Conventional Solution Synthesis

Carbon *gem*-polyhalides are a big family of organic compounds endowed with two or more halogen atoms in a single carbon atom and, therefore, a large variety of compounds are embraced in this definition. In this section, we will review those *gem*-polyhalides used as precursors or intermediates in on-surface synthesis, namely $-CX_3$, $-CHX_2$ and $=CX_2$, which have previously been employed in conventional wet chemistry, for a variety of purposes, including their synthesis, use as synthetic intermediates and applications (see **Figure 1**).

2.1. Trifluoromethyl Group (-CF_3)

As quoted by M. Schlosser, the group -CF_3 "*doesn't grow on trees*". Indeed, there are not any natural trifluoromethylated species on earth: all are human-made.[23] Regarding the synthesis of trifluoromethylated aromatic molecules (Ar-CF_3), several methods have been reported to introduce the CF_3 substituent in an aromatic ring.[24] With just a few exceptions, all of them have in common the use of copper to trap the generated CF_3 ions in situ and, finally, to substitute the corresponding arene, which should contain in turn a suitable leaving group. It is important to highlight the pioneering work of McLoughlin and Thrower, who described the synthesis of perfluoroalkyl-substituted aromatic compounds from iodoarenes, using CF_3I in the presence of copper powder.[25] Later, in 1991, Urata and Fuchinami were able to functionalize different aromatic iodides by using the Ruppert-Prakash-type reagent (CF_3-$SiEt_3$)[26,27] and employing CuI, under stoichiometric conditions.[28] Since then, alternative sources of the CF_3 ions have been reported, such as a sulfonium ylide[29] and the Togni reagent,[30] to substitute aromatic iodides and boronic acids, respectively. Interestingly, aromatic amines can undergo a copper-promoted Sandmeyer trifluoromethylation reaction,[31] allowing the synthesis of different Ar-CF_3 molecules. Recently, Zao and MacMillan have achieved the trifluoroalkylation of a broad range of aryl bromides using metalla-photoredox conditions.[32]

We can certainly state that, among all the substituents discussed herein, CF_3 has been the most exploited one and its use has caused a tremendous impact in both life and materials sciences. Indeed, its applications in drug discovery have been widely described. Interestingly, a recent review has highlighted that since the first drug containing the CF_3 substituent was FDA-approved in 2002, 19 new drugs have been commercialized having this group.[33] It is today acknowledged that the CF_3 group displays some important features that favorably impact in the biological activity, chemical reactivity and physico-chemical behavior of the host molecule, namely its size, lipophilicity, electrostatic interactions, and electronegativity.[34] Furthermore, in the agrochemistry field, the presence of CF_3 substituents is frequent in herbicide molecules, thanks to the increase of their lipophilicity, which improves its capacity to cross the cellular membranes of plants. Moreover, the CF_3 group protects the molecule against the intrinsic metabolic action of the plant, thus increasing the durability of the herbicide.[35]

The trifluoromethyl group has also found applications in organic electronics since its excellent electron-withdrawing ability enhances the electronic properties and improves the stability of the corresponding organic material, thus extending its potential applications in photovoltaics.[36]

2.2. Trichloro- and Tribromomethyl Groups (-CCl_3 and -CBr_3)

Two major methods to synthesize these *gem*-tribromides and trichlorides have been described. Starting from a molecule that contains a CF_3 group and making it to react with different Lewis acids, such as BX_3,[37] FeX_3,[38] AlX_3, or SiX_4.[39] Alternatively, Ar-CCl_3 entities can also be synthesized by reacting a formyl group at the aromatic moiety with PCl_5 and AIBN,[40] while the Ar-CBr_3 analogues can be photo-thermally generated by reacting a simple methyl substituent with NBS and AIBN in presence of a tungsten lamp.[41]

Nevertheless, when compared to their trifluorinated homologues, there are fewer reported applications of these carbon trihalides, likely due to their higher instability. For instance, both Ar-CCl_3 and Ar-CBr_3 are prone to decompose to the

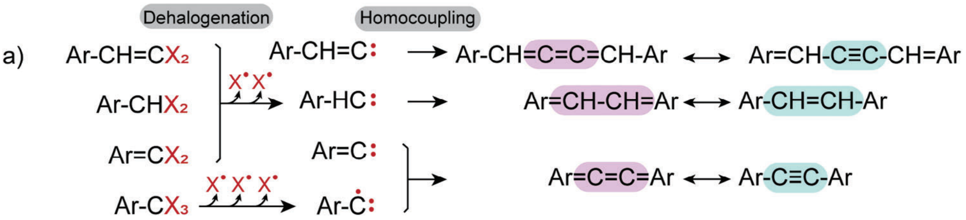

Figure 2. Mechanism of synthesis of molecular nanocarbons by activation of carbon *gem*-polyhalides.

corresponding carboxylic acids under basic conditions.[42] In fact, Ar-CCl_3 entities can be useful intermediates for the synthesis of tri-allyl derivatives, under catalytic conditions.[43] Regarding Ar-CBr_3, they have been used as building blocks for the wet synthesis of quinazolines,[44] octacarboxylated spherosilicates,[45] and for constructing polymers[46] by copper catalysts, providing the generation of triple bonds.

In addition to the aromatic species, diverse molecules containing *gem*-tri-halogenated substituents have also been synthesized and further employed as useful synthetic intermediates. For instance, α-tribromomethylamines,[47] α-trichlorocarbinols,[48] and β-tribromomethyl nitroalkanes[49] can be prepared by reacting the nucleophilic species CX_3^-, generated from chloroform or bromoform, with imines, carbonyls, or nitroalkenes, respectively.

2.3. Dibromomethyl Group (-$CHBr_2$)

Aromatic $CHBr_2$ molecules have mostly been synthesized through the Wohl-Ziegler method, by reacting a methyl group with Br_2 or NBS in presence of a radical initiator as light, AIBN or benzoyl peroxide.[50,51] Interestingly, they can also be synthesized from the corresponding aldehyde by employing different methodologies.[52,53] Regarding their applications, they are known to undergo Diels-Alder reactions, acting both as diene or dienophile, depending on the chemical nature of the molecule.[54,55] In a pioneering work, Sygula and Rabideau were able to synthesize the first fragment of the C_{60} fullerene in a non-pyrolytic way, by using a molecule with different CBr_3 substituents.[56] After this initial discovery, these authors[57] and Siegel[58] were able to synthesize the corannulene fragment of C_{60} using similar strategies. Finally, these $CHBr_2$ substituents have also been useful for achieving the synthesis of diverse amazing carbon nanostructures, including heptacenes,[59] helicenes,[60–62] and carbon-nanobelts.[63,64]

2.4. *Gem*-Dibromoalkene Group (=CBr_2)

Molecules endowed with *gem*-dibromoalkenes are known since 1962, when F. Ramirez and coworkers carried out the reaction of benzaldehyde with carbon tetrabromide and

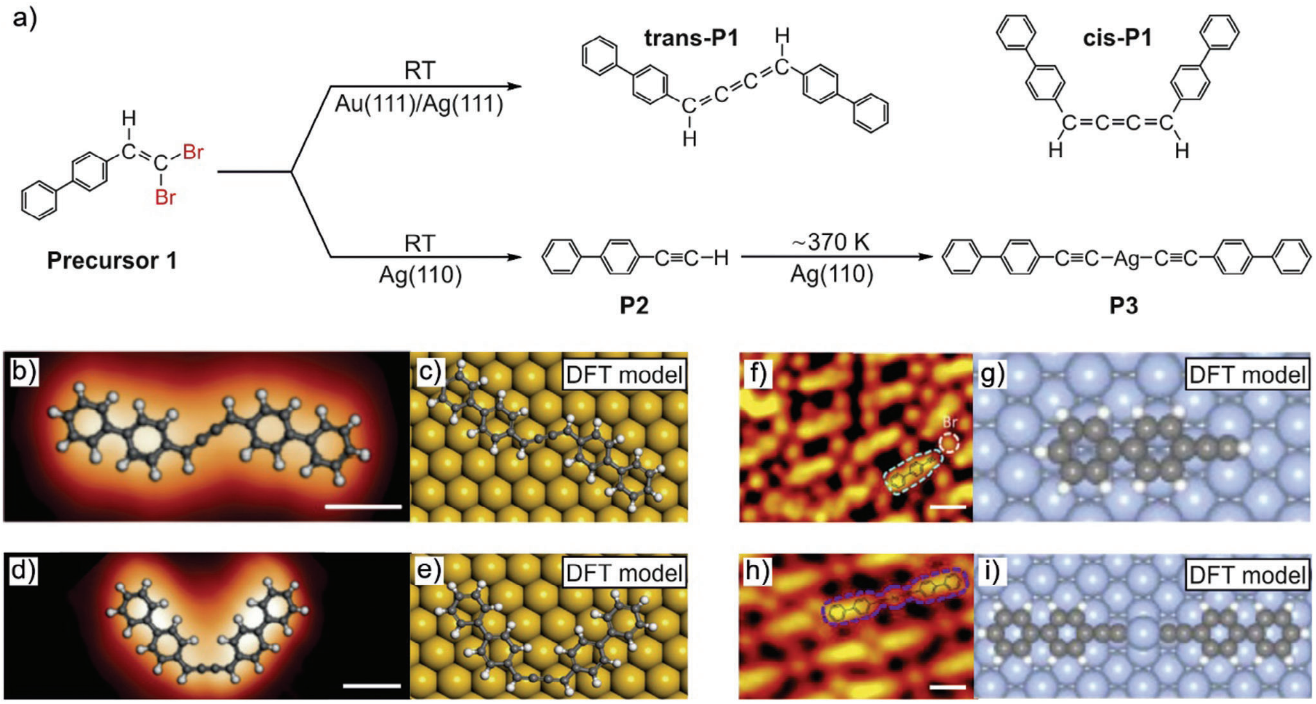

Figure 3. Seminal activation of gem-dibromovinylene on noble metals. b–e) Reproduced (Adapted) with permission.[10] Copyright 2017, Wiley. f–i) Reproduced (Adapted) with permission.[90] Copyright 2021, American Chemical Society.

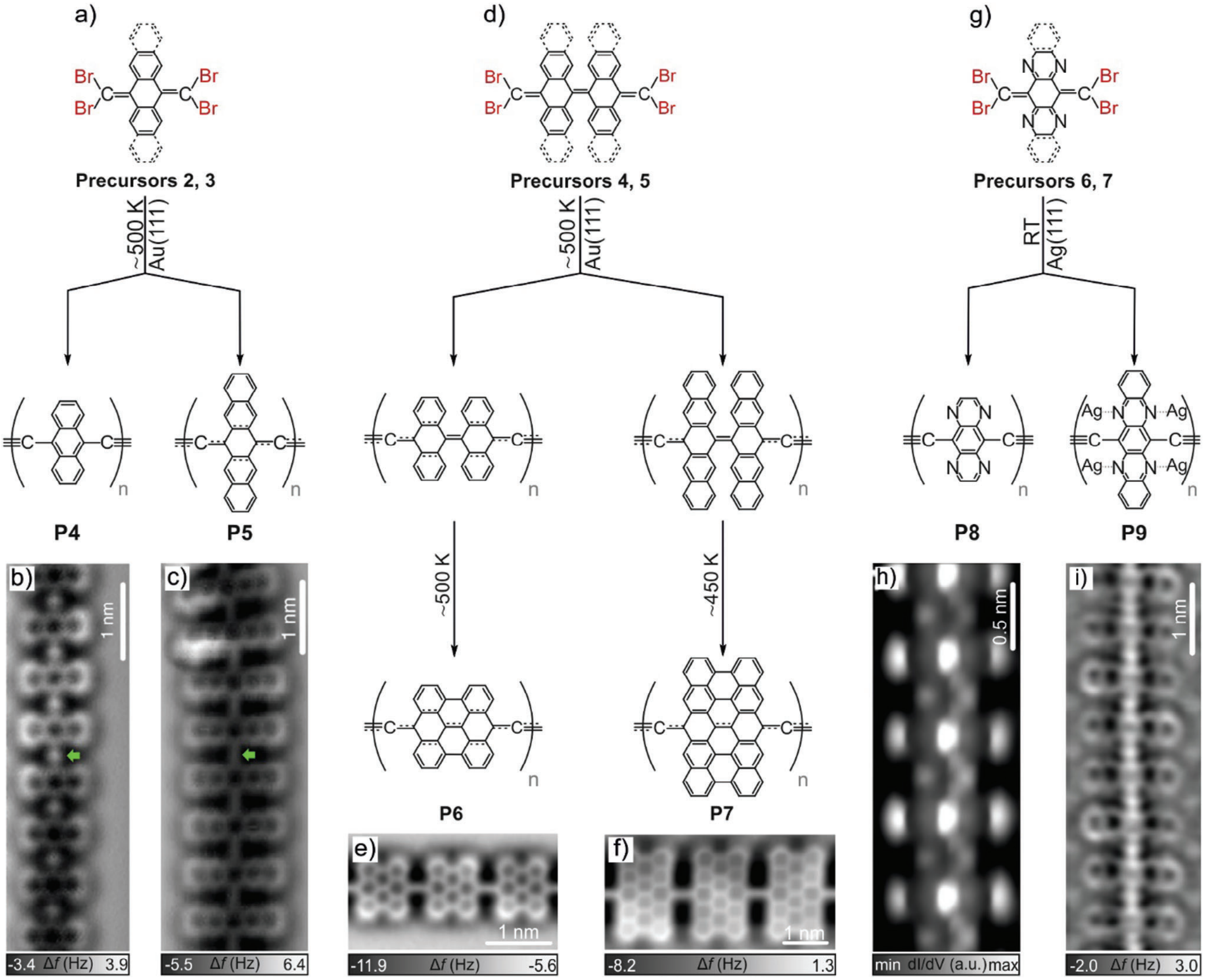

Figure 4. On-surface synthesis of acene- and periacene-based polymers. a–e) Reproduced (Adapted) with permission.[96] Copyright 2020, Nature Publishing group. d,f) Reproduced (Adapted) with permission.[97] Copyright 2020, Wiley. g,h) Reproduced (Adapted) with permission.[98] Copyright 2023, Wiley. g,i) Reproduced (Adapted) with permission.[99] Copyright 2022, Wiley.

triphenylphosphine, leading to (2,2-dibromovinyl)benzene.[65] Interestingly, further lithiation of *gem*-dibromoalkenes undergo Fritsch-Buttenberg-Wiechell (FBW) rearrangement to yield the corresponding alkyne.[66–68] In 1972, the Nobel laureated E. J. Corey gathered both reactions to transform carbonyl groups into alkynes, in a sequential way known as the Corey-Fuchs homologation reaction.[69]

Since then, molecules bearing *gem*-dibromoalkenes have been widely used in different fields. However, it has been in organic electronics where these molecules have found the most success. As a representative example, *gem*-dibromoalkenes allowed to R. Tykwinski and coworkers the synthesis of polynes as models to obtain the sp-carbon allotrope known as carbyne. By synthesizing a series of varying length polyynes (from n = 1 to 22 repeating units) and measuring their optoelectronic properties, it was determined the HOMO-LUMO gap of carbyne in 2.56 eV.[70,71] Furthermore, application in organic solar cells has also been reported through the synthesis of light harvesting tetra[60]fullerene nanoarrays. In this example, the multistep synthetic procedure affording the nanoarray stems from the previously reported diformyl functionalized oligomer which, eventually, gives the intermediate *gem*-dibromoalkene by reaction with CBr_4 and PPh_3 according to Corey's procedure. An organic photovoltaic device fabricated from this nanoarray and poly(3-hexylthiophene) showed an external quantum efficiency of 15% at 500 nm.[72]

gem-Dibromoalkenes have also been useful intermediates in the total synthesis of some natural products. Thus, remarkable examples are the synthesis of the diacetylenic spiroacetal enol ether AL-2, which showed antitumor activity,[73] the natural insecticide Azadirachtin,[74] whose synthesis took 22 years, as well as the antibiotics α- and β-Lipomycin.[75]

Interestingly, when *gem*-dibromoalkenes are embedded into a *p*-quinoid unit, the resulting products are tetrabromo-*p*-quinodimethanes (TBQs). Due to the steric hindrance between the bromine atoms and the *peri*-hydrogens, a highly distorted geometry out of the planarity is obtained for these molecules,

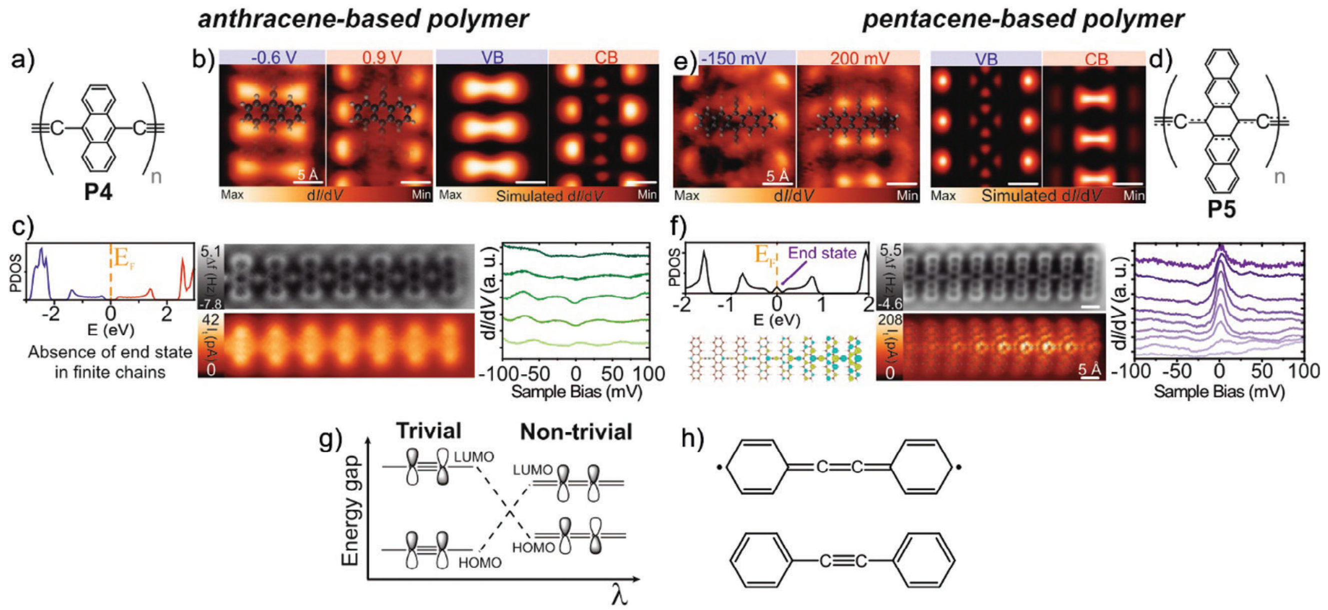

Figure 5. Emergence of non-trivial quantum phases of matter in acene-based polymers. a–f) Reproduced (Adapted) with permission.[96] Copyright 2020, Nature Publishing Group.

adopting a butterfly shape. The presence of the four reactive bromine atoms and the singular geometry of these TBQs makes them ideal and versatile building blocks for different purposes, depending on their substitution pattern. For instance, the quinoid character of these building-blocks has been useful for the synthesis of π-extended analogues of Thiele's and Chichibabin's hydrocarbons, as well as some open-shell character molecules.[76] More recently, it has also been possible to induce transitions between the close and open-shell character by using different methodologies.[77]

TBQs have also found application in photovoltaics. Thus, new hole transporting materials (HTMs) have been synthesized by introducing triarylamine functionalities into an anthraquinone-based TBQ, affording high photovoltaic performance and stability in large area Perovskite Solar Cells (PSCs).[78] In addition, TBQs have been used as platforms for synthetizing advanced materials exhibiting aggregation-induced emission (AIE) and photochromism, similarly to the well-known tetraphenylenes, due to the steric hindrance exerted by their *peri*-hydrogens.[79–81] More recently, it has been described the synthesis of different linked TBQ dimers,[82] with up to eight bromine atoms, which may enhance the properties of the previously described TBQ monomers.

When the core of the TBQ is a pentacene, the presence of phenyl substituents yields a structure that is prone to undergo a cyclodehydrogenation reaction to provide hexabenzocoronenes that have potential as semiconducting materials for transistor applications.[83] Finally, the introduction of suitable functional groups in the phenyl rings of TBQ, has allowed the synthesis of electrically conductive metal[84] and covalent organic frameworks.[85]

Despite the interest of the aforementioned uses of *gem*-polyhalides as starting or intermediate compounds for a variety of purposes, their application in on-surface covalent synthesis of carbon nanomaterials represents an unprecedented application of these functional groups, as described in the following section.

3. Carbon Polyhalides for on-Surface Synthesis of Carbon Nanomaterials

Carbon monohalides have played a pivotal role in the on-surface synthesis of carbon nanomaterials by the promotion of the Ullmann coupling reaction[6] and, recently, on the formation of carbocycles thanks to tip-induced chemistry.[86–88] Alternatively, carbon *gem*-polyhalides like $-CHBr_2$,[89] $=CBr_2$,[10,12,90] $-CBr_3$,[11] $-CCl_3$,[91] and $-CF_3$[92] have recently been exploited for engineering molecular compounds of distinct dimensionality.

In the following, we review the aforementioned three distinct strategies on surfaces to trigger chemical reactions on molecular precursors endowed with carbon *gem*-polyhalides functional groups.

3.1. On-Surface Synthesis by Thermal Annealing

Thermal annealing of suitably functionalized organic precursors is the most common stimulus employed to promote the synthesis of molecular nanocarbons on surfaces. In some works, using precursors endowed with *gem*-polyhalides functional groups, theory was used to shed light about the reaction mechanisms.[11,12,89–91] Herein, the activation mechanism of these precursors and subsequent homocoupling is less explored and exhibits some peculiarities when compared to the well-known reactivity of carbon monohalides driving the so-called Ullmann coupling.[6,14] Concerning carbon monohalides, after deposition of the precursors on the surface, such Ullmann reaction first involves the dissociation of the halogens by surface reactivity, followed by the formation of surface-stabilized radicals. Depending on the nature of the species and the substrate, they can undergo a homocoupling reaction forming new C-C bonds, or, alternatively, form intermediates based on carbon-metal-carbon bonds, which, in favorable cases, upon subsequent annealing can afford the desired C–C couplings by the release of the bridging metal adatom.[6,14] Regarding *gem*-polyhalides, as schematically illustrated in the left panel of **Figure 2**, the first step of the mechanism consists of a dehalogenation process generating a mono-radical, with a theoretical energy cost accessible in experimental conditions (ranging from 0.01 to 0.91 eV). Next, in most cases, a subsequent dehalogenation step follows the process, with an activation energy from 0.1 to 0.75 eV, forming a carbenoid reaction intermediate. When the precursor is a trihalide, the last dehalogenation step leads to the formation of a carbynoid radical intermediate. Note that all these intermediates are highly reactive and are stabilized by the metal substrates, anticipating the key role of the adatoms and the important catalytic properties of metallic surfaces. Further efforts will be necessary to elucidate the complete picture of such role. The last step is a homocoupling reaction of the carbenes (or carbynes) intermediates, resulting in the formation of distinct cumulenes, polyenes or polyynes bonds (see right panel in Figure 2). Alternatively, a different reaction pathway was proposed for porphyrins bestowing $-CF_3$ termini, in which first a defluorination was suggested, followed by $=CF_2$ to $=CF_2$ homocoupling, to end up with a final stepwise full dehalogenation.[92]

Historically, getting inspiration of the alkyl monohalides employed for demonstrating the Wurtz reaction on surfaces,[7] the gem-dibromoalkene functional group was equipped at one of the terminus of a biphenyl molecule (**Precursor 1**), as illustrated in **Figure 3**. Its deposition on Au(111) or Ag(111) surfaces afforded the full debromination and homocoupling reaction, rendering the formation of **trans-P1** and **cis-P1** cumulene-like products.[10] Remarkably, analogous experiments on Ag(110) led to debromination and passivation by residual hydrogen at room temperature (**P2**, see Figure 3f,g) and the final expression of silver-directed organometallic dimers (**P3**, see Figure 3h,i) upon annealing.[90] Here, it is worth to point out that $\mathbf{C_2Br_4}$ (as intermediate from $\mathbf{CBr_4}$ precursor) and $\mathbf{C_4Br_4}$ species were able to trigger the expression of organometallic polyynes.[93,94]

Triggered by the extensive research on the synthesis of acene and periacene families on surfaces, an anthracene-like proaromatic precursor was successfully equipped with two dibromoalkene ($=CBr_2$) moieties, affording the 11,11,12,12-tetrabromoanthra-*p*-quinodimethane precursor, termed **Precursor 2** (see **Figure 4a**), which was strategically thought for allowing the engineering of linear anthracene-based polymers (**P4**, see Figure 4a,b).[12]

The deposition of a submonolayer of **Precursor 2** on Au(111) and annealing to 500 K results in the formation of relatively long and defect-free polymers (**P4**, see Figure 4b), without any trace of residual bromine atoms. In the last decade, high-resolution non-contact atomic force microscopy (nc-AFM) imaging with a CO-functionalized tip has been shown to provide submolecular resolution[4] and even to discriminate bond order.[95] Applying such technique to elucidate the chemical structure of **P4**, it is revealed that such polymer is based on anthracene moieties linked by ethynylene bridges, with the triple bond being distinctly identified as a bright protrusion[11] at an appropriate tip-sample distance (see green arrow in Figure 4b). The concordance between experimental and simulated nc-AFM images confirms the presence of the ethynylene bridge. Remarkably, these wires exhibit considerable flexibility, accommodating open curvatures up to 130° through minor bending of the ethynylene linkages. The robustness of the bonds is evident in their ability to withstand tip-induced lateral manipulations, altering polymer curvature while preserving the chemical structure. This resilience suggests promising applications in the field of flexible electronics. At this annealing stage, these polymers lose their terminal carbon atoms and are passivated by residual atomic hydrogen, rendering in the formation of anthracene-ending polymers.

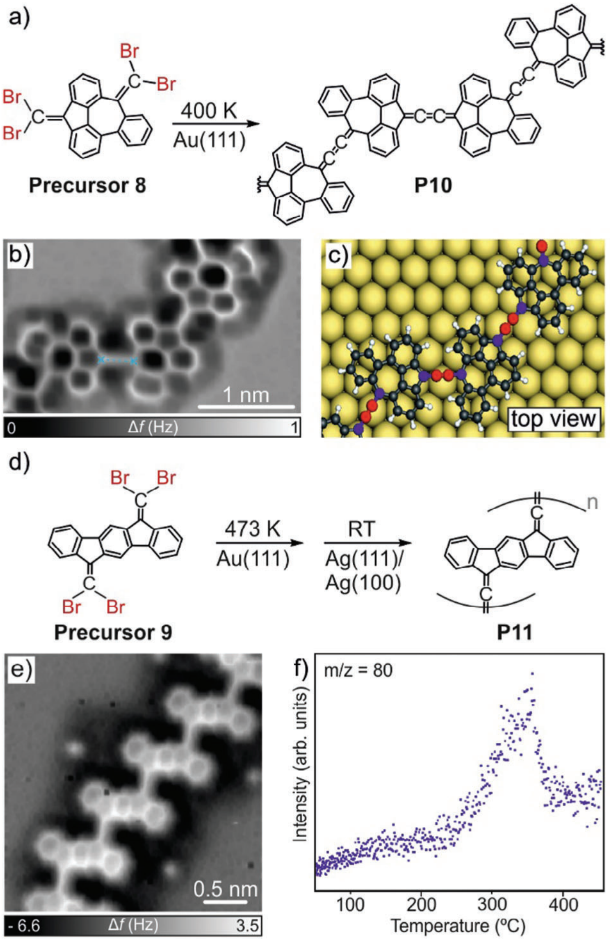

Figure 6. Synthesis of cumulene-linked 1D non-benzenoid π-conjugated polymers. a–c) Reproduced (Adapted) with permission.[105] Copyright 2020, Wiley. d–f) Reproduced (Adapted) with permission.[106] Copyright 2021, Royal Society of Chemistry.

Steered by the success in taking advantage of the $=CBr_2$ functional group to promote the formation of ethynylene-bridged anthracene polymers, next logical step was to equip the same functional group to highly interesting proaromatic species from the acene and the periacene families. To this aim, a pentacene derivative, known as 6,13-bis(dibromomethylene)–6,13-dihydropentacene (see Figure 4a) and termed here as **Precursor 3**, was prepared. The deposition of a submonolayer coverage on a clean Au(111) substrate held at room temperature, followed by annealing at 500 K affords the formation of extensive 1D

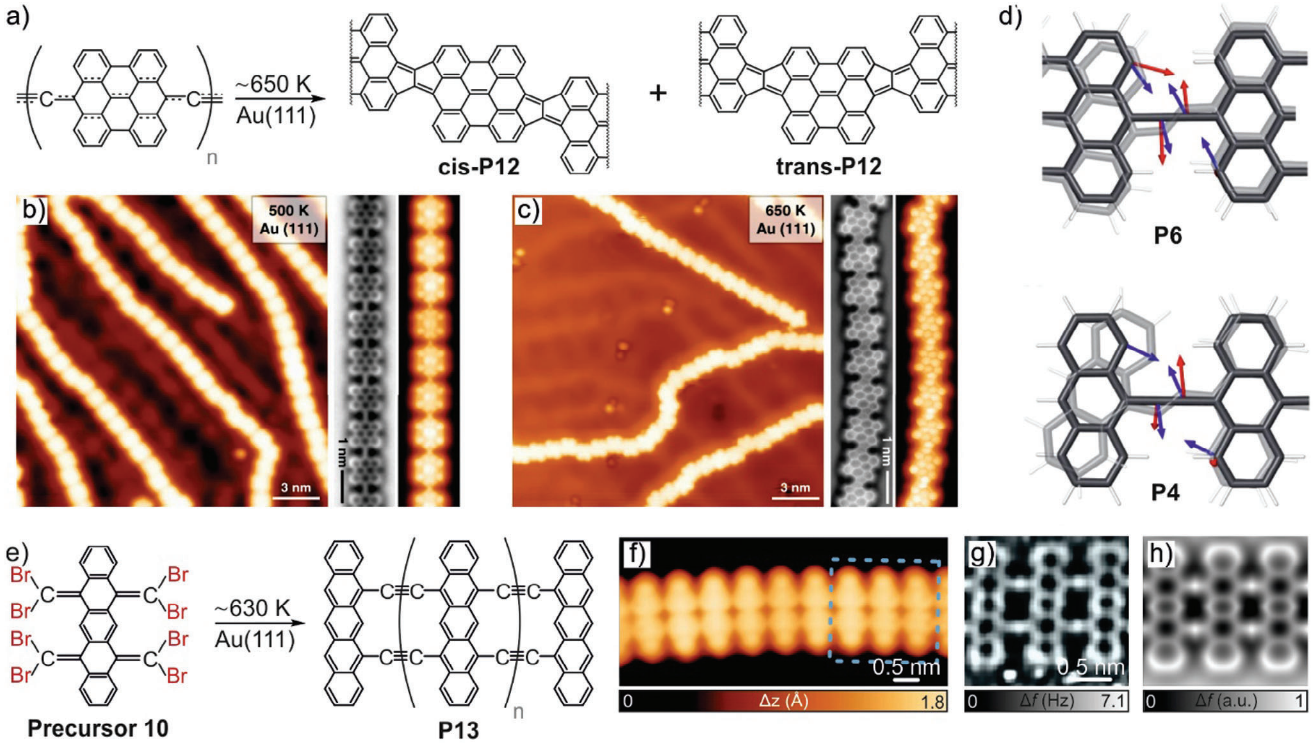

Figure 7. On-surface synthesis of π-conjugated ladder polymers. a–d) Reproduced (Adapted) with permission.[107] Copyright 2022, Wiley. e–h) Reproduced (Adapted) with permission.[111] Copyright 2020, Royal Society of Chemistry.

polymers (**P5**).[96] By high resolution nc-AFM measurements with a CO-functionalized tip, the constituent monomers could be identified as pentacene moieties, while the whole polymer exhibited a planar adsorption. Importantly, pentacene units were interconnected by linear bridges, which were not exhibiting a bright protrusion in the middle (see green arrow in Figure 4c), a feature that could be rationalized by comparison with theory as a change in the dominant resonant form, moving from ethynylene-aromatic in the case of anthracene to a more cumulene-quinoid one for the pentacene-based polymers. Further impetus was provided by the synthesis of 10,10′-bis(dibromomethylene)−10H,10′H-9,9′-bianthracenylidene, termed **Precursor 4**, which by deposition on Au(111) and subsequent annealing at 500 K gave rise to the formation of long 1D polymers (**P6**) (see Figure 4d).[96] As illustrated by high-resolution nc-AFM imaging with a CO-functionalized tip (see Figure 4e), the polymers are planar and formed by bisanthene moieties linked by linear bridges, which do not show an enhancement in the frequency shift signal, and thus by an analogous rationalization as in the pentacene case (DFT and experimental evidence) are considered as cumulene-like bridges. Herein, the annealing protocol has promoted the sequential debromination, homocoupling and cyclodehydrogenation reactions. An analogous strategy was employed by the design of 13,13′-bis(dibromomethylene)−13*H*,13′*H*-6,6′-bipentacenylidene, named **Precursor 5** (see Figure 4d), whose on-surface synthesis on Au(111) affords the formation of cumulene-bridged peripentacene polymers (**P7**) (see Figure 4f).[97]

Once it was shown that all-carbon 1D π-conjugated ethynylene/cumulene-bridged polymers could be synthesized on surfaces, the next natural step was to synthesize heteroatom-containing precursors. Two contemporary studies addressed the synthesis of 11,11,12,12-tetrabromo-1,4,5,8-tetraaza-9,10-anthra-*p*-quinodimethane (named **Precursor 6**, Figure 4g) and 11,11,12,12-tetrabromo-1,4,5,8-tetraaza-9,10-anthra-*p*-quinodimethane (termed **Precursor 7**, Figure 4g), which on Ag(111) led to the formation of N-containing ethynylene-bridged covalent (from **Precursor 6**) and coordination (from **Precursor 7**) polymers, termed **P8** and **P9**, respectively (see Figure 4h,i).[98,99]

In order to gain insight into the electronic structure of these promising families of π-conjugated acene- and periacene-based polymers, scanning tunnelling spectroscopy (STS) was performed over the molecular wires, allowing the elucidation of the electronic bandgap and the spatial distribution of the onsets of the valence and conduction bands by comparison with DFT simulations of free-standing polymers. In detail, polymers **P4**[12] (see **Figure 5a–c**) and **P9**[99] displayed bandgaps of 1.5 eV and 1.0 eV, respectively, whereas polymers **P5**[96] (see Figure 5d–f), **P6**[96] and **P7**[97] exhibited low bandgaps in the range of 0.3 – 0.8 eV.

Notably, over the last decades there has been a revolution in our understanding of condensed matter physics by the introduction of the topological band theory.[100] Herein, the Su–Schrieffer–Heeger (SSH) model afforded the rationalization of the electronic properties of conducting polyacetylene,[101] a seminal example of 1D π-conjugated polymer, and revealed two distinct topological quantum classes, i.e., the trivial and the non-trivial one, featuring each of them a distinct value of the specific topological invariant. Inspired by such findings, the evolution of both the bandgap and the topological quantum class, via Z_2 invariant,[96,102,103] of the family of all-carbon ethynylene-bridge acene polymers was theoretically inspected by increasing the size of acenes from benzene to nonacene, revealing a size-dependent topological phase transition. The polymers based on shorter monomers (benzene and anthracene) are topologically trivial, whereas the polymers comprising longer monomers (pentacene, heptacene and nonacene) are topologically non-trivial.[96,97] The hallmark proof for a topological phase transition will be the inversion of the bands and the presence of edge states. In fact, the ethynylene-bridge anthracene polymers do not exhibit end states, as expected for a standard topologically trivial semiconductor, whereas the pentacene-based polymers display an end state, which is clearly manifested in DFT calculations of a free-standing polymer and corroborated by STM (see Figure 5c vs Figure 5f). Furthermore, as expected, there was an inversion on the shape of the valence and conduction bands for both polymers. Thus, it was demonstrated the feasibility of inducing a topological phase transition in π-conjugated polymers by manipulating the monomer size. The increase of the monomer size leads to a shift in the dominant resonant form of the polymer, thereby modifying its topological class and unveiling the intricate connection between topology and resonant forms. The family of periacenes were also theoretically predicted to be topologically non-trivial for monomers equal or bigger than bisanthene, and experimentally corroborated for bisanthene and peripentacene polymers. Notably, the length of the polymer was also shown to be a variable crucial for topological phase transitions. The seminal work on cumulene-bridged pentacene polymer identified a topological phase transition for pentacene polymers comprising more than 25 monomers on Au(111), being assigned the origin of such transition to a length-dependent pseudo Jahn Teller effect.[104]

At this point, it is essential to mention the relation between the resonant form of the polymer and its topological quantum class.[96] Notably, there are different bonding characters of the frontier HOMO and LUMO orbitals on the bridging unit, as shown in Figure 5g. In one case, the frontier orbital has a strong bonding character, while the other has antibonding nature. Thus, the occupation of these frontier orbitals determines the resulting resonant form of the bridging unit. Namely, if the HOMO orbital has a bonding character, the bridging unit adopts a -C≡C- ethynylene form. In contrast, the antibonding character of HOMO promotes the cumulene-like =C=C= character of the bridging unit (see Figure 5h). Moreover, the energy levels of the bonding/antibonding orbitals may swap according to external conditions, such as the character of the aromatic units or the length of the polymer. Therefore, the crossing level of these two orbitals will define the quantum phase transition between the two different π-resonant structures of the polymer. In terms of solid state physics based on the SSH model, it represents a topological phase transition, where the non-trivial topological phase is manifested by the emergence of in-gap edge states strongly localized at the terminals of the polymer, as discussed previously. It is also worth noting that the proximity of the crossing level of two frontier orbitals, by definition, reduces the band gap of the polymer. This paves the way to design a new class of low-bandgap polymers without the necessity of heterogeneous doping.

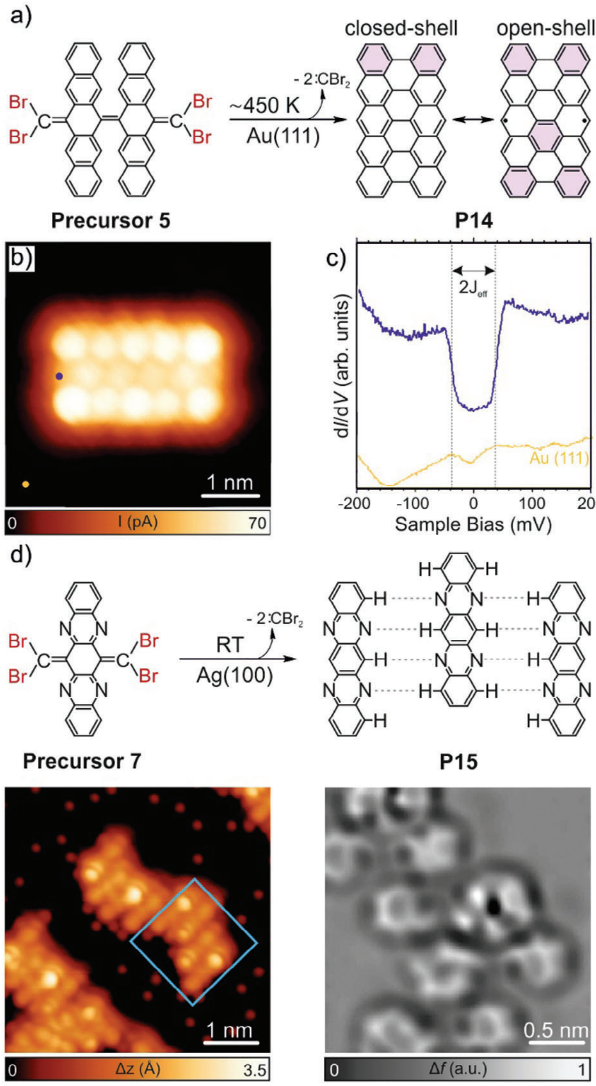

Figure 8. On-surface synthesis of nanographenes by debromination and passivation with residual hydrogen from precursor species bestowing = CBr_2 terminal moieties. a–c) Reproduced (Adapted) with permission.[112] Copyright 2021, American Chemical Society. d) Reproduced (Adapted) with permission.[99] Copyright 2022, Wiley.

The *gem*-dibromoalkene group also proved to be an effective tool for synthesizing unique π-conjugated polymers when incorporated into selected species containing odd-membered rings. On one hand, a molecular precursor equipped with = CBr_2 moieties on five- and seven-membered rings, termed **Precursor 8** (see **Figure 6a**), yielded π-conjugated cumulene-bridged non-benzenoid polymers (**P10**, see Figure 6b,c) upon deposition and annealing at 400 K on Au(111), featuring an electronic bandgap of 1.6 eV .[105] Similarly, an indenofluorene backbone substituted with peripheral gem-dibromoalkene groups (**Precursor 9**, see Figure 6d) produced cumulene-bridged indenofluorene polymers (**P11**, see Figure 6e) on Au(111), Ag(111), and Ag(100),

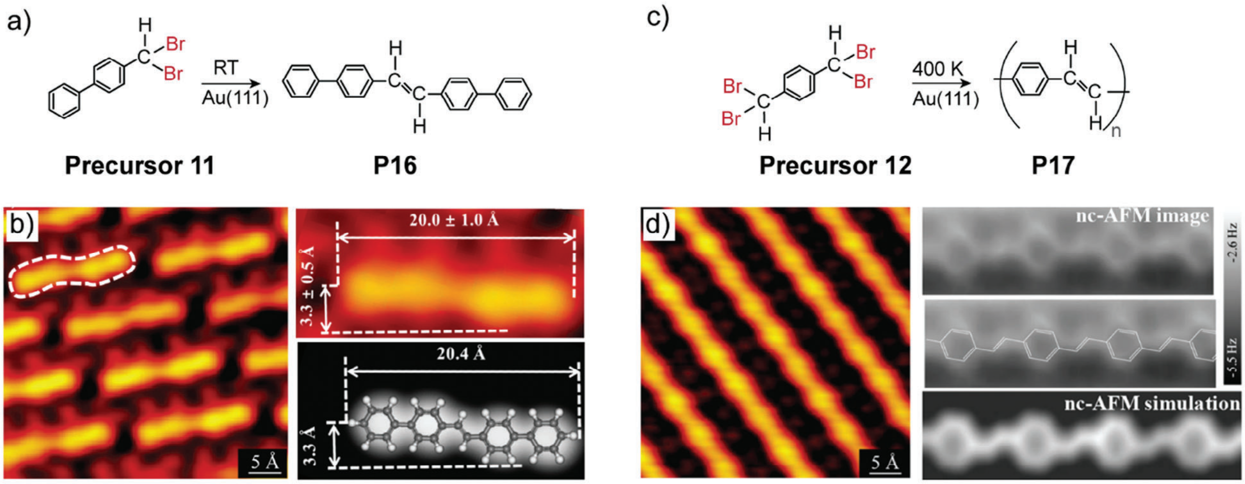

Figure 9. Synthesis of carbon nanomaterials via activation of dibromomethyl groups on Au(111). a–d) Reproduced (Adapted) with permission.[89] Copyright 2018, American Chemical Society.

displaying a bandgap of 1.25 eV on Au(111).[106] Additionally, temperature programed desorption (TPD) experiments depicted the desorption of HBr molecules from the Au(111) surface, and thus the concomitant bromine atoms, with a maximum desorption rate at 360 °C (see Figure 6f).

A next step in dimensionality involved the engineering of conjugated ladder polymers. Here two distinct strategies were employed: i) ladderization, and ii) exploiting multiple connectivity from initial precursors. The first method, termed ladderization, is a process in polymer science by which 1D polymers are transformed into quasi-unidimensional conjugated ladder polymers. Such protocol was initially tried by annealing ethynylene-bridged polymers (**P4**) on Au(111), which resulted in irregular polymers.[107,108] Surprisingly, reproducing the same strategy on cumulene-bridged bisanthene polymers (**P6**) triggered a unique ladderization reaction that afforded pentalene-bridged bisanthene polymers (**cis-P12** and **trans-P12**, see **Figure** 7a–c),[107] which fulfils the Glidewell and Lloyd's[109,110] rules for aromaticity of non-benzenoid polymers. Importantly, the theoretical studies about the mechanisms behind the annealing processes of anthracene and bisanthene polymers (**P4** and **P6**, respectively) reveal that specific vibrational modes triggered such ladderization for the latter polymer, altogether indicating that not only the transition state but also the internal vibrational modes of the reactant might play an important role in reaction mechanisms on surfaces (see Figure 7d). In line with this ladderization strategy, the annealing of nitrogen-containing **Precursor 7** to 373 K on Au(111) or to 473 K on Ag(111)[99] gave rise to the coexistence of linear and zigzag pyrrolopyrrole π-conjugated ladder polymers exhibiting a bandgap of 2.2 eV on Au(111). Such findings were expanded by the study of a shorter tetra-aza linker, i.e., **Precursor 6**, on Ag(111), where the ladderization reaction afforded the subsequent pyrrolopyrrole π-conjugated ladder polymer at 313 K.[98] The second method to synthesize ladder polymers is based on designing precursors bestowing multiple $=\mathrm{CBr}_2$ functional groups. To exemplify such strategy, a pentacene derivative equipped with four functional dibromoalkene groups (5,7,12,14-tetrakis(dibromomethylene)–5,7,12,14-tetrahydropentacene, termed **Precursor 10**, see Figure 7e), was deposited on Au(111) and annealed to 630 K, giving rise to a doubly-linked conjugated ladder polymer (**P13**, see Figure 7e,h), which is based on ethynylene bridges and features a relatively low bandgap of 0.57 eV.[111]

Concerning the $=\mathrm{CBr}_2$ functional group, it is also worth to mention that it has been feasible to detach it from the precursor and passivate the species with residual hydrogen as illustrated in **Figure** 8, affording the formation and study of nanographenes such as peripentacene (**P14**, see Figure 8a,b), demonstrating its open-shell character (see Figure 8c),[112] or tetraazapentacene (**P15**, see Figure 8d).[99]

Contemporarily to the use of $=\mathrm{CBr}_2$ units, the dibromomethyl group ($-\mathrm{CHBr}_2$) was equipped in the terminus of a biphenyl derivative and the resulting species (dibromomethyl)–1,1′-biphenyl, named **Precursor 11**, were deposited on Au(111) to form *trans*-4,4-diphenylstilbene, termed **P16** (see **Figure** 9a).[89] Importantly, the bridge between the phenyl moieties was tentatively identified as a vinylene group (see Figure 9b). Next logical step was based on the synthesis of a linear precursor endowing two dibromomethyl units in *para* positions, namely 1,4-bis(dibromomethyl)benzene, termed **Precursor 12**, whose deposition on a pristine Au(111) held at room temperature and subsequent annealing at 400 K afforded the formation of phenylenevinylene (PPV) chains, named **P17** (see Figure 9c,d).[89] Herein, now the link between phenyl moieties was imaged by nc-AFM as a staggered line with crossing angle ≈120°, and undoubtedly assigned to vinylene. An on-surface mechanism for the activation of *gem*-alkyl dibromides was proposed based on a two stepwise debromination and subsequent homocoupling reaction.

In parallel to the previous works exploiting *gem*-dibromoalkene ($=\mathrm{CBr}_2$) and alkyl dihalide ($-\mathrm{CHBr}_2$) functional groups, molecular precursors were endowed with carbon *gem*-trihalides functional groups maximizing the number of halides. Three successful approaches introduced the $-\mathrm{CBr}_3$,[11] $-\mathrm{CCl}_3$,[91] $-\mathrm{CF}_3$[92] moieties for on-surface synthesis. On one hand, tribromomethylbenzene (**Precursor 13**) was prepared,

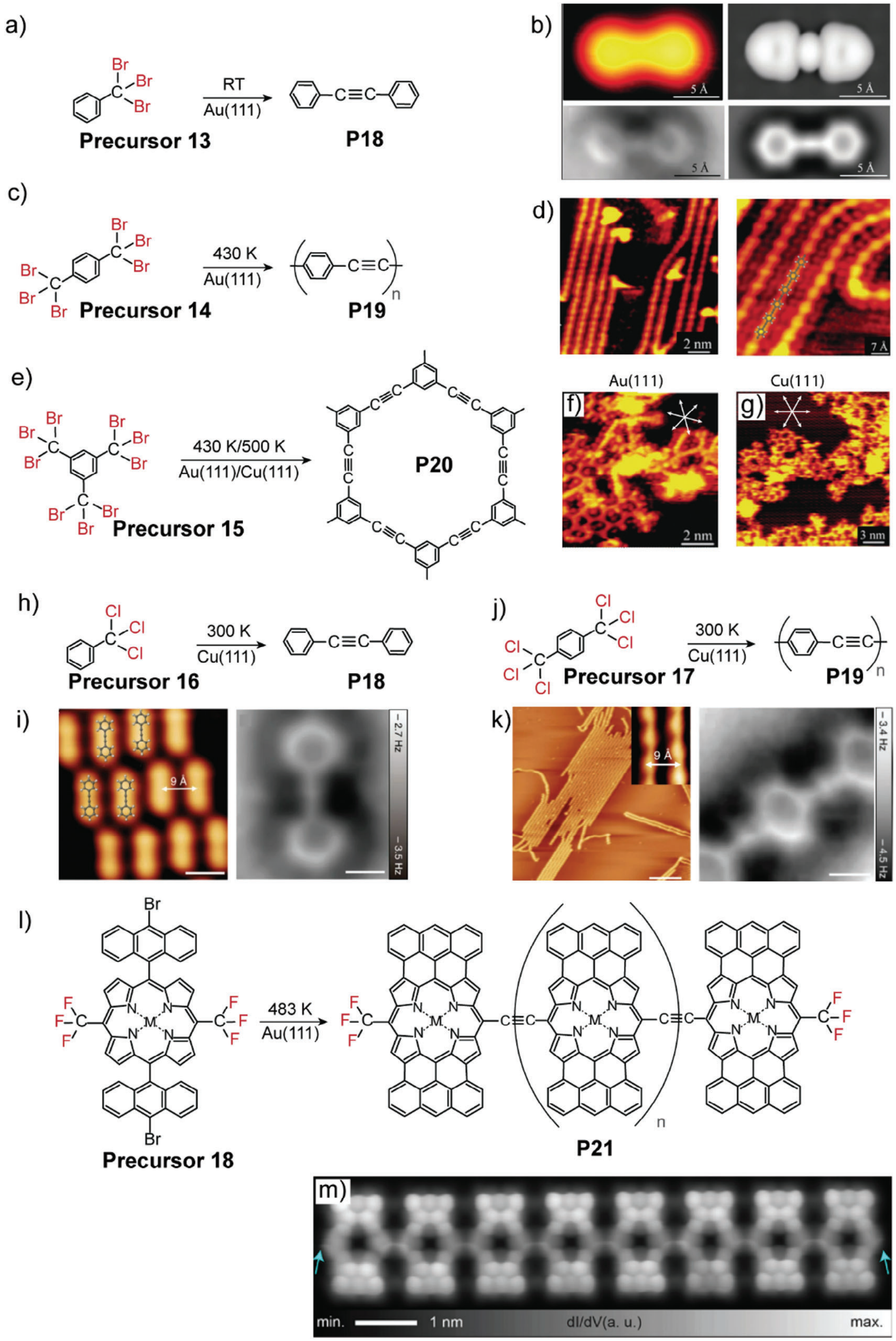

Figure 10. On-surface synthesis by activation of carbon trihalides on surfaces. a–g) Reproduced (Adapted) with permission.[11] Copyright 2018, Wiley. h–k) Reproduced (Adapted) with permission.[91] Copyright 2018, Nature Publishing Group. l,m) Reproduced (Adapted) with permission.[92] Copyright 2022, Wiley.

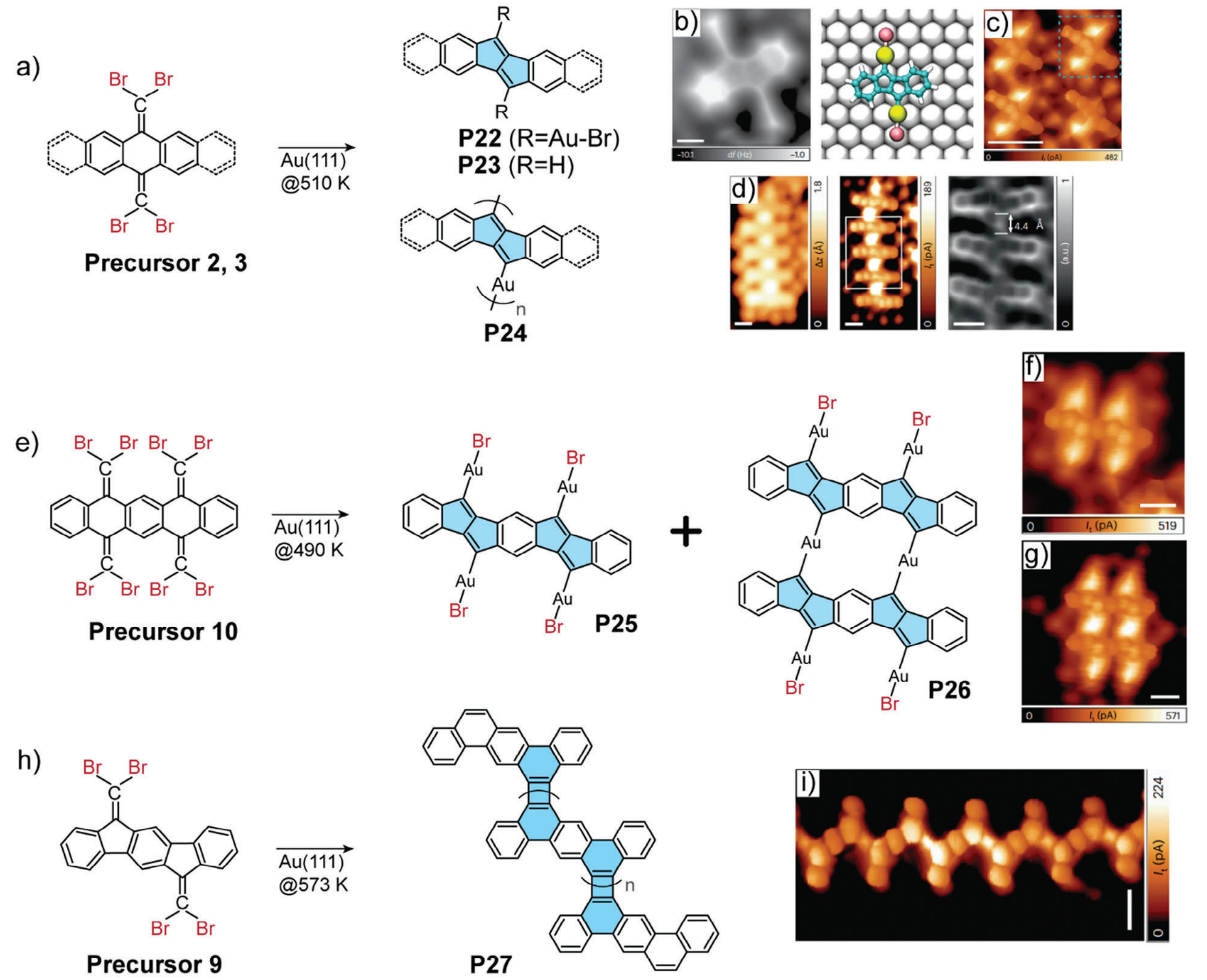

Figure 11. On-surface synthesis of π-conjugated compounds by hot substrate deposition of precursors equipped with =CBr_2 moieties. a–i) Reproduced (Adapted) with permission.[114] Copyright 2023, Nature Publishing Group.

whose deposition on Au(111) held at RT afforded the covalent dimer **P18** (see **Figure** 10a,b), demonstrating the envisioned full dehalogenation and homocoupling of **Precursor 13**. Subsequently, 1,4-bis(tribromomethyl)benzene (**Precursor 14**) was synthesized, which, upon deposition on Au(111) and annealing to 430 K, afforded poly(arylene ethynylene) chains, termed **P19** (see Figure 10c,d).[11] Wisely, the threefold functionalization of benzene with –CBr_3 units led to the synthesis of 1,3,5-tris(tribromomethyl)benzene (**Precursor 15**), which gave rise to small covalent 2D patches, named **P20** on both Au(111) and Cu(111) surfaces (see Figure 10e–g). Notably, in the three cases, the bridges between monomers were based on ethynylene linkers. An analogous strategy was exemplified by using trichloromethylbenzene, named **Precursor 16**, and 1,3-bis(trichloromethylbenzene), termed **Precursor 17**, on Cu(111), leading to reaction products **P18** and **P19**, respectively (see Figure 10h–k).[91]

Additionally, a porphyrin derivative bearing two –CF_3 groups at trans positions was successfully synthesized (**Precursor 18**) and deposited on Au(111).[92] In a two-step process of annealing (433 K and 483 K), a porphyrin polymer based on ethynylene bridges was reported (**P21**, see Figures 10l,m). As aplausible mechanism, a first debromination and passivation with hydrogen of two pristine bromo-anthracene moieties as well as cyclohydrogenation is suggested, finally followed by dehalogenative homocoupling of the carbon polyhalides. Importantly, the termini of the polymers could be visualized and assigned to intact –CF_3. Such finding was crucial for being able to form polymers comprising distinct metal centers by simply depositing and annealing in stepwise fashion Cu-, Co- and Pd-metalated precursors.

3.2. On-Surface Synthesis by Landing of Precursors on a Hot Substrate

The temperature of the substrate has been previously reported to play a decisive role in selecting reaction pathways.[113] Motivated from such findings, **Precursors 2, 3 and 10** were deposited on Au(111) kept at high temperature (≈500 K), which

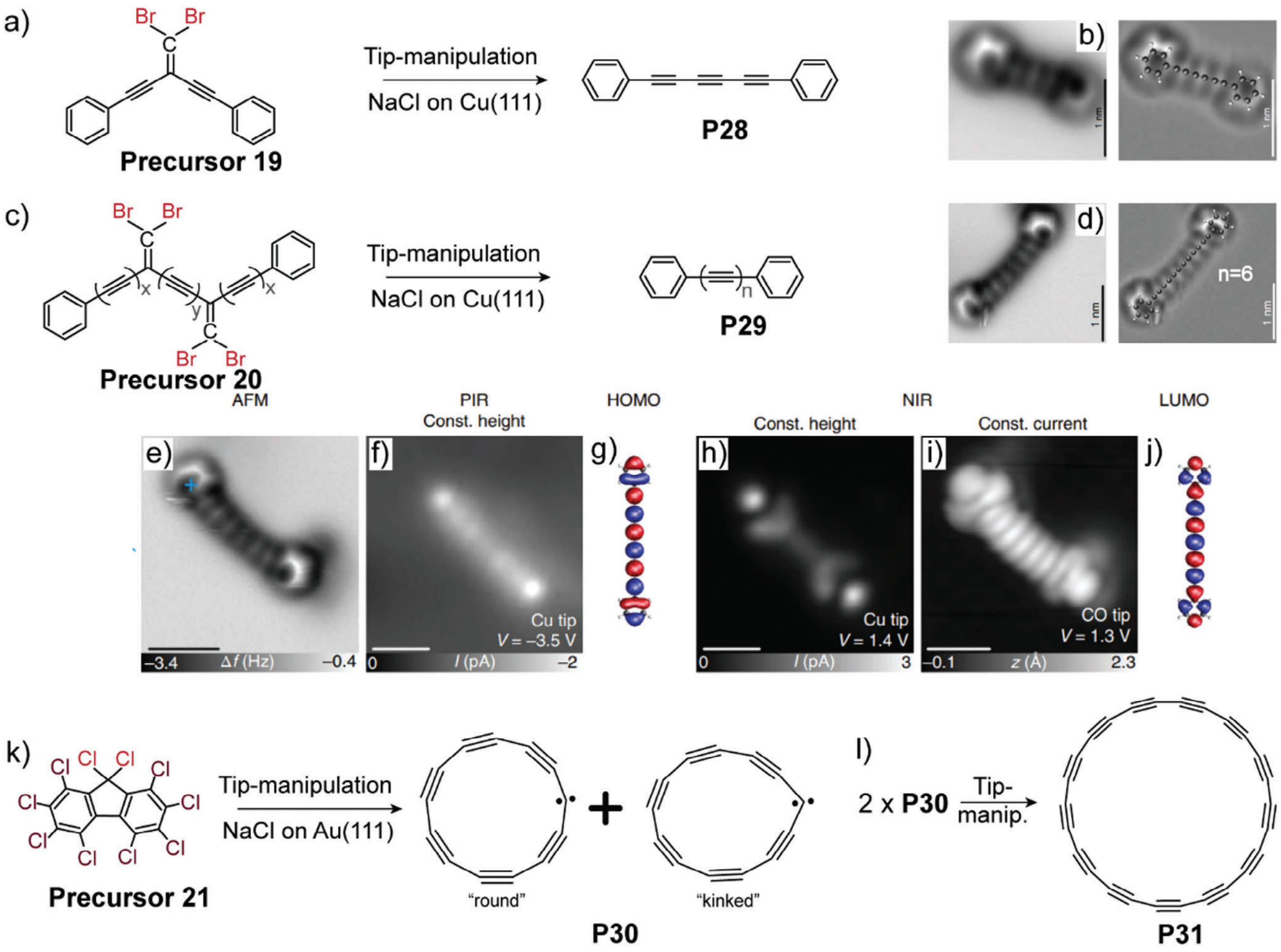

Figure 12. On-surface synthesis of polyynes by skeletal rearrangement induced by atomic manipulation on precursors bestowing carbon dihalides. a–j) Reproduced (Adapted) with permission.[120] Copyright 2018, Nature Publishing Group. k,l) Reproduced (Adapted) with permission.[121] Copyright 2024, Science.

led to an internal structural rearrangement of the species affording the inclusion of antiaromatic pentalene moieties in the monomer backbones, giving rise to the formation of diacenopentalene derivatives (see **Figure** 11a–g).[114] In detail, three distinct type of constituents could be detected, namely organometallic monomers (**P22**) or monomers passivated by hydrogen (**P23**), and organometallic polymers (**P24**). Additionally, the deposition of **Precursor 10**, endowed with four $=CBr_2$ groups, gives rise to the formation of organometallic monomers and dimers incorporating two pentalene moieties per unit (**P25** and **P26**). DFT and quantum mechanics/molecular mechanics (QM/MM) simulations were carried out to elucidate the reaction mechanism of the generation of pentalene subunits, taking as a seminal example **Precursor 2**. In a first step, one of the $=CBr_2$ suffers a C-Br cleavage assisted by a gold adatom, releasing one bromine atom, while simultaneously swapping positions with the remaining Br atom and forming a linear –C-Au-Br motif. Subsequently the same process happens to the remaining $=CBr_2$ functional group. Next, the two carbon atoms incorporate into the monomer backbone sequentially, affording the formation of very reactive benzynes. As a final stage, the intermediate compound suffers an intramolecular FBW rearrangement[66–68] giving rise to pentalene moieties, in which the apical carbons of the five-membered moieties are still bonded to Au-Br entities. Such final product can stay intact on the surface (**P22**), or suffer debromination, which is then followed by organometallic polymerization (**P24**) or directly passivation with residual hydrogen (**P23**).

An extension of such strategy, but this time bearing the $=CBr_2$ functional group in a five-membered ring of an indenofluorene-based precursor (**Precursor 9**), afforded the design of π-conjugated ladder polymers of dibenz[a,h]anthracene units linked by antiaromatic cyclobutadiene segments, termed **P27** (see Figure 11h,i). Here, it is proposed a mechanism by which once the carbon atoms from the functional group have been incorporated into the molecular backbone, forming highly reactive benzynes, and thanks to the presence of gold adatoms a homocoupling reaction between adjacent benzynes results in the formation of the cyclobutadiene linkages.

3.3. Tip-Induced Chemistry

The tip of an STM has frequently been used to induce elementary steps of a chemical reaction.[2] Actually, a carbon monohalide, iodobenzene, was seminally used to exemplify the formation of biphenyl on a Cu(111) substrate thanks to tip-induced debromination and homocoupling via lateral manipulation with the STM tip.[115] Recently, molecular precursors incorporating monohalides have gained momentum in the on-surface synthesis community allowing to design by tip-induced chemistry previously precluded molecular species.[116–118] Herein, the emerging area of elusive carbocycles[86–88,119] has also benefited from such strategy.[87,88,119]

Concerning the *gem*-dibromoalkene functional group, prolineal precursors of distinct length equipped with $=CBr_2$ (**Precursor 19** and **Precursor 20**, see **Figures** 12a,c) were successfully tailored manipulated by an STM tip affording the synthesis of polyynes of distinct length (**P28** and **P29**)[120] as illustrated in Figures 12b,d. Both PIR (positive ion resonance) and NIR (negative ion resonance) of **P29** could be measured, revealing a decrease in the energy of the PIR for longer polyynes, and exhibiting an excellent agreement with theoretical simulations (see Figure 12e–j). Additionally, by tip-induced manipulation C_4Br_4 species could be transformed into diyne moieties.[93]

Recently, the CCl_2 and CCl groups of a decachlorofluorene species (**Precursor 21**) were manipulated with a STM tip affording the formation of the first odd-membered carbocycle (C13, termed here **P30**), which displays distinct conformation geometries, being two of them able to react whenever they are in proximity producing the[26] carbocycle (C26, named **P31**, see Figures 12k,l).[121]

Altogether, tip-induced chemistry anticipates potential impact in the synthesis of carbon-based nanomaterials while using the precursors described along the review.

4. Conclusions and Outlook

In summary, carbon *gem*-polyhalides have emerged as successful reactive groups for steering covalent reactions on surfaces, resulting in atomically precise 0D compounds, π-conjugated 1D polymers, quasi-1D ladder polymers, and 2D nanoarchitectures, while exhibiting a variety of appealing structural, electronic, and topological properties.

Three distinct chemical approaches to activate the *gem*-polyhalides are reviewed. The most successful and traditional paradigm for on-surface synthesis relies on deposition of a submonolayer coverage of the precursor and subsequent annealing to a desire temperature. Following this approach, it was reported the successful activation of distinct *gem*-polyhalides: $–HCBr_2$, $=CBr_2$, $-CBr_3$, $-CF_3$, $-Cl_3$, affording homocoupling in between species, and even ladderization reactions upon further thermal stimuli. Importantly, distinct families of monomers were introduced in such polymerization processes including all-carbon or heteroatomic acenes, periacenes and porphyrins. The findings were not only limited to on-surface synthesis, since important discoveries bridging physics and chemistry realms were found, such as establishing the relation between the topology of the electronic band structure and the resonant form of a polymer, or the relevance of vibrational modes on surfaces to drive reaction pathways.

A second approach to trigger the *gem*-polyhalides into surface-confined chemical reactions is based on the sublimation on precursors equipped with $=CBr_2$ moieties on hot substrates to stimulate unexpected intramolecular reactions, thus affording individual products, organometallic compounds and quasi-1D π-conjugated ladder polymers. Herein, the generation of antiaromatic units have also allowed the synthesis of hybrid aromatic/antiaromatic systems.

Ultimately, tip-induced atomic manipulation has enabled dehalogenation, and, by triggering carbon skeletal rearrangements, afforded the creation of exotic carbon allotropes, including the elusive carbocycles.

Up to now, distinct, and innovative π-conjugated polymers have been produced by on-surface synthesis, some of them displaying unique and intriguing topological non-trivial nature. We anticipate the use of these fertile functional groups in monomers of distinct structure to construct periodic 2D networks in the near future. Additionally, there is a need to explore the potential of directing similar reaction pathways by harnessing carbon *gem*-polyhalides on semiconducting or insulating materials. Furthermore, significant research endeavors are expected to elucidate the role of various synthetic stimuli, such as light or electron-beam irradiation. In this context, optical spectroscopy and transport characterization will play crucial roles. Concurrently, the ongoing quest involves leveraging these π-conjugated nanomaterials for device applications through a dual approach: either transferring them onto technologically relevant supports or directly encapsulating them under ultra-high vacuum conditions to protect the fabricated nanomaterials from environmental degradation. Regardless of the chosen approach, a promising future lies ahead for the utilization of diverse chemical structures featuring carbon *gem*-polyhalides as highly versatile and efficient functional groups, contributing to further advancements in the burgeoning field of on-surface covalent synthesis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

π-conjugated polymers, gem-polyhalides, on-surface synthesis, scanning probe microscopy, skeletal rearrangement

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