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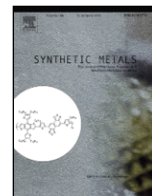
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Molecular engineering in 2D surface covalent organic frameworks: Towards next generation of molecular tectons - A mini review

Corentin Pigot, Frédéric Dumur *

Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397, Marseille, France

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ABSTRACT

Molecular engineering on surface has been revolutionized by the possibility to create covalent connections between molecular tectons. Following the pioneering works on supramolecular structures and their triumphal developments during a decade, covalent organic frameworks on surface open up new routes towards robust and regular porous macromolecular structures usable in practical applications such as molecular electronics, energy conversion or catalysis. Metal surfaces can be also be decorated with semiconducting organic structures, widening the scope of applicability of these polymer-modified surfaces. If the first generation of molecular building blocks was designed so that the functional groups were introduced for a specific reactivity, recently, a breakthrough has been achieved in 2016 and 2017 with the almost simultaneous reports of ENA and INDO4 capable to initiate different reaction pathways depending of the surface topography or the surface coverage. Prior to these two works, in 2015, another exciting candidate (i.e. TAPB) exhibiting however a more limited range of reactivity than ENA or INDO4 was reported, its reactivity being based on the presence of acetyl end-groups. In this minireview, the intriguing properties of these unique building blocks are presented.

1. Introduction

During the last two decades, functionalization of surfaces with organic molecular tectons has triggered a great deal of efforts from both physicists and chemists. This intense research activity is supported by the wide range of applications in which these two-dimensional structures can be used, ranging from (photo)catalysis, gas and energy storage, energy conversion and membrane applications [1–8]. Since the seminal work of Grill and coworkers on surface covalent organic frameworks (sCOFs) obtained by an Ullmann cross-coupling reaction of halogenated molecular tectons [9–15], a wide range of chemical reactions have been examined to elaborate monolayered sCOFs [16]. In these different works, specific functional groups have been selected to induce a predetermined reaction, even if unexpected reactions have sometimes been reported in the literature, especially with metal surfaces, the underlying surface acting as a catalyst [17]. For all these monomers, different parameters can be modified to optimize the efficiency of the on-surface reaction, as exemplified by the polymerization temperature, the deposition rate, the concentration or the substrate choice. These different parameters constitute effective tools to drastically reduce the number of defects and improve the polymerization rate. However, at a few exceptions, the expected reaction occurs.

Besides, if the expected reaction occurs, the reaction output can sometimes be controlled by mean of other parameters such as the presence of an additional reagent that can temporarily act as a template favouring a reaction over another one. A remarkable example has been reported in 2019 on the Ullmann coupling reaction of 1,4-bis(6,6'-dibromo-[2,2':6',2''-terpyridin]-4'-yl)benzene (p-DBTB) on Au(111) substrate. If an uncontrolled Ullmann coupling between molecular tectons occurred at 430–661 K, orientation of the terminal pyridines of p-DBTB could be efficiently controlled while depositing p-DBTB on Au(111) substrates prefunctionalized with iron atoms. By complexing the terpyridine cavity with pre-evaporated iron atoms, Fe(II) terpyridine complexes could form on the surface, orientating both the pyridines of p-DBTB and arranging the monomers linearly. As a result of this intermediate template, π -conjugated nanoribbons comprising sexipyridine units could be finally obtained upon annealing of the surface at 508–705 K and desorption of iron atoms [18]. In the same spirit, the on-surface growth of the Sierpiński triangle fractals could be carefully governed by the water content acting as a regulator equilibrium during the dehydration reaction of diboronic acids [19]. Besides, if the presence of scavengers (water, metal atoms) could modify the reaction output, the reactivity of monomers remained unchanged, halogenated tectons still giving rise to Ullmann coupling and boronic acids to the for-

* Corresponding author.

E-mail addresses: corentin.pigot@univ-amu.fr (C. Pigot); frederic.dumur@univ-amu.fr (F. Dumur)

mation of boroxines by dehydration. As a next generation of molecular tectons, molecular building blocks that can initiate different coupling modes carefully controlled by the choice of the surface, the surface topography or the surface coverage are eagerly awaited, as these monomers promise flexibility and versatility (See Scheme 1).

Indeed, from a synthetic point of view, these tectons are appealing candidates as an unique synthesis is required to obtain a versatile molecule giving access to various macromolecular organic structures on surface. Especially, the coupling mode and thus the final architecture of the macromolecular structure can be selected "on demand" by mean of a pre-programmed reactivity. To date, only three molecules namely 6-ethynyl-2-naphthoic acid (ENA), *s*-indacene-1,3,5,7(2*H*,6*H*)-tetrone (INDO4) and 1,3,5-*tris*(4-acetylphenyl)benzene (TAPB) offering such a reactivity have been reported in the literature. In this short review, an overview of these molecules is presented.

1.1. Reactivity of 6-ethynyl-2-naphthoic acid (ENA)

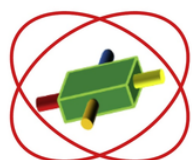
Pioneering works concerning the design of elemental building blocks of multiple reactivities were reported in 2016 by Studer and coworkers [20]. Interestingly, 6-ethynyl-2-naphthoic acid (ENA) proved to be highly versatile as the reaction outcome could varied with the surface coverage or the topography. The dimer of ENA i.e. 1,4-buta-1,3-diynylbis(2-naphthoic acid) (BDNA) could form via a surface-assisted Glaser coupling reaction. Indeed, one specificity of the on-surface reactions is the possibility to perform chemical transformations that could not be carried out in solution phase chemistry. One of the most relevant examples in this field is the polymerization of alkanes via

a C—H bond activation by the substrate [21]. But the covalent linkage of porphyrins by C—H bond activation on Cu(110) surfaces can also be mentioned [22]. In this last case, complexity of the polymer growth was clearly evidenced, C—C intermolecular bond formation resulting from the subtle interplay between, surface energy, steric effects, molecule diffusion on surface and surface-assisted reaction resulting from a catalytic effect from the metal. Recently, two remarkable examples of C—H bond activation by carefully controlling the steric hindrance and the positions of the activating groups of dibromo-meta-terphenyl derivatives could selectively induce a dehydrogenative coupling or the combination of a dehydrogenative coupling and a debrominative coupling [23]. Concerning naphthalene, the possibility to form C—C bonds by a surface-assisted decarboxylation of 2,6-naphthalenedicarboxylic acid was reported prior to this work [24]. However, in the context of this study, no on-surface decarboxylation of ENA was observed on Au(111) substrates but an unprecedented dehydrogenative coupling of acids, leading to the formation of *bis*-acylperoxides (See Scheme 2). Interestingly, dehydrogenative coupling of ENA was observed even upon annealing a supramolecular phase of ENA at 124 °C under low coverage conditions, furnishing BDNA and providing a two-dimensional (2D) metal-carboxylate coordination polymer (see Fig. 1.1). On the opposite, the same reaction carried out at high molecular density on Au(111) substrates provided the co-existence of two phases, the first one corresponding to the formation of bis(alkynyl)Au complex stabilized by a dense network of hydrogen bonds, the second one corresponding to 1D polymers derived from BDNA and comprising monomeric units connected by mean of *bis*-acylperoxides (see Fig. 1.2). A significant disorder could be found on the surface, with the presence of linear polymer chains connected by mean of Au(carboxylate) complexes. To improve the reaction selectivity (i.e. formation of linear chains over branching), an Au(100) surface was chosen due to its channel-structured topography. Using these substrates, branching was suppressed and linear polymer chains extending over 100 nm could be imaged on the surface. A distance of 1.08 nm between parallel rows of polymer chains was determined, corresponding to the distance imposed by the channel-structured surface.

Investigations of the chemical mechanism on surface by depositing a preformed BDNA structure revealed the formation of *bis*-acylperoxide linkage to occur at room temperature, demonstrating the butadiyne central part of BDNA to provide unique properties favouring the formation of *bis*-acylperoxide groups. If the mechanism was not fully understood in 2016, the dimerization of ENA was determined as occurring prior to the dehydrogenative coupling of the acid end-groups. In 2017, the mutual influence between carboxylic groups and terminal alkynes was evidenced by the same group who studied the reactivity of 2,6-naphthalenedicarboxylic acid (NDCA) and 4,9-*bis*-(trimethylsilyl)ethynyl)anthracene co-deposited onto Ag(111) or Au(111) surfaces [25]. In this work where the carboxylic group and the silylated alkynes are attached onto two different monomers, the ability of the carboxylic groups of NDCA to induce a deprotection of the silane groups of the anthracene derivative via the formation of silyl esters was successfully demonstrated, this reaction resulting from a σ -bond metathesis. Using this unprecedented strategy, a supramolecular network of desilylated anthracene could be obtained on Ag(111) surface and thermal annealing of the surface at 120 °C could provide anthracene-based oligomers resulting from a dehydrogenative homocoupling (Glaser coupling) between molecular tectons. While replacing the Ag(111) surface by an Au(111) surface, the cascade reaction combining σ -bond metathesis and Glaser coupling furnished oligomers of elongated length compared to that obtained on Ag(111) substrates. However, this result could only be obtained while annealing the surface at a higher temperature, namely 170 °C.

Following this initial work on Au surfaces, the same authors newly examined the reaction outcome of ENA but on a different surface i.e.

Traditional molecular tectons



Molecular tectons with a unique coupling mode

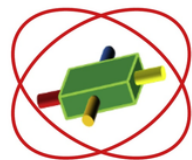


unique coupling mode

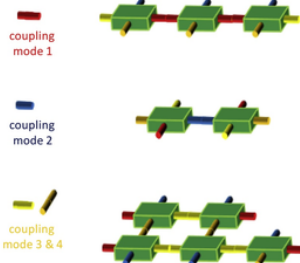
No Selection rules. Same coupling irrespective of:

- Temperature
- Surface topology
- Surface coverage
- etc....

Advanced molecular tectons



Molecular tectons with four different coupling modes



coupling mode 1

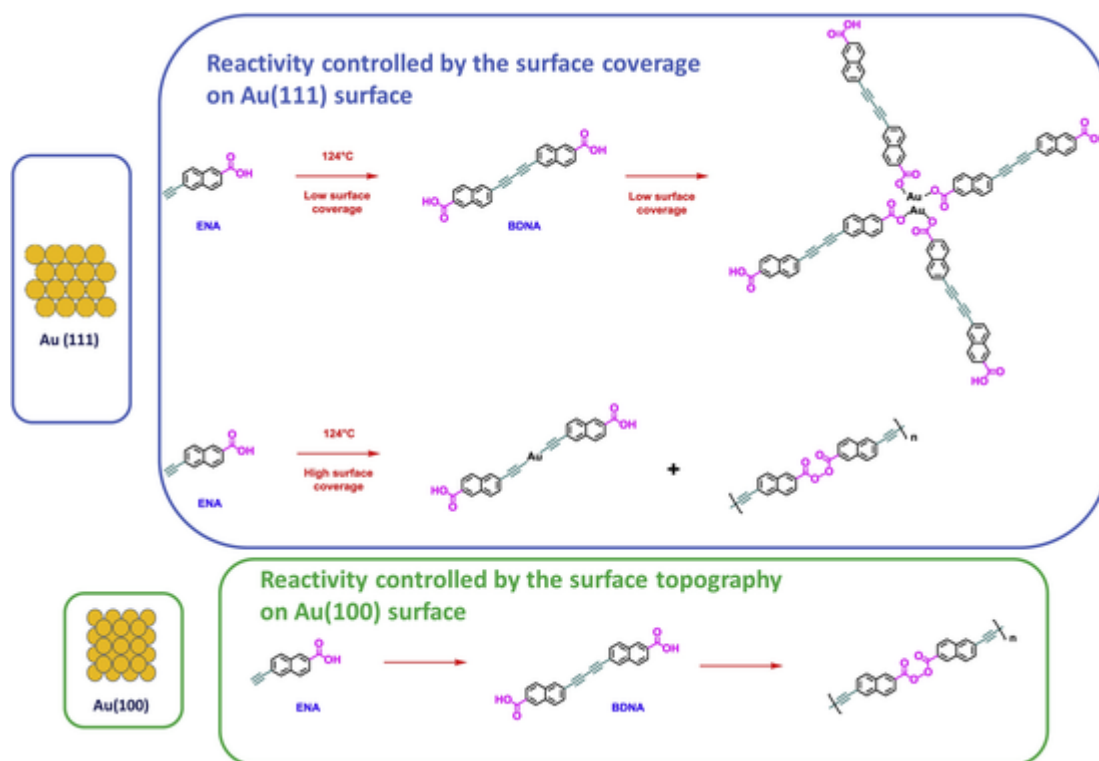
coupling mode 2

coupling mode 3 & 4

Selection rules between coupling modes

- Temperature
- Surface topology
- Surface coverage
- etc....

Scheme 1. The main difference between a traditional molecular tecton and the second generation of monomers allowing to discriminate between different coupling modes by mean of external parameters.



Scheme 2. The different reaction pathways of BDNA depending of the surface coverage and topography.

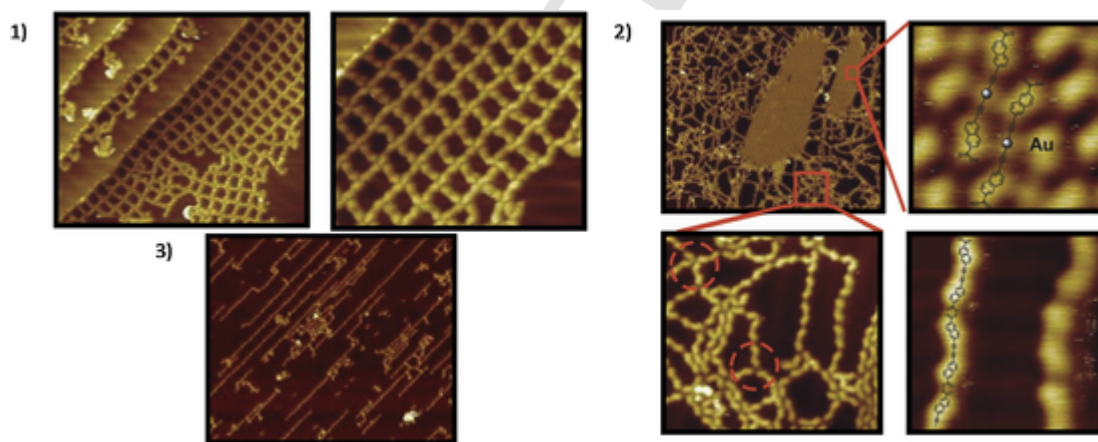
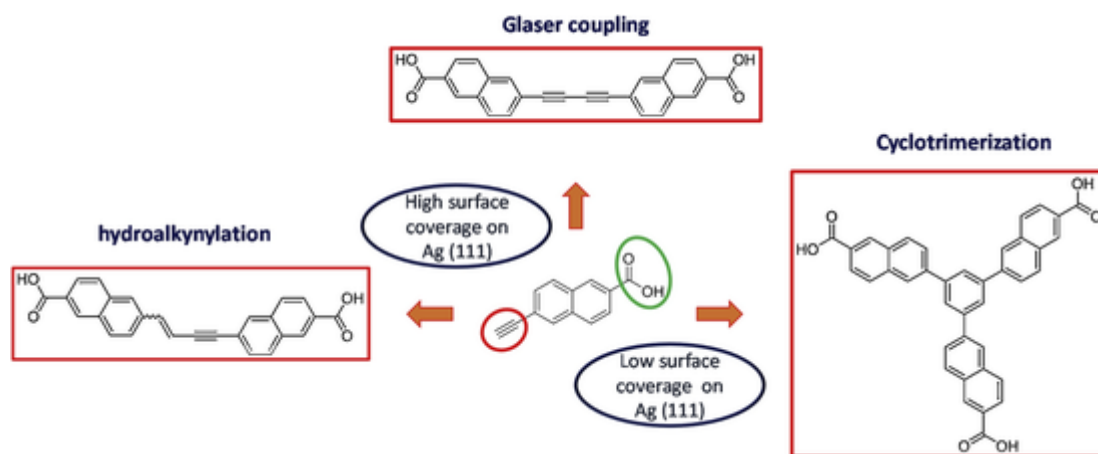


Fig. 1. STM Images on Au(111) surface of 1) the two-dimensional (2D) metal-carboxylate coordination polymer of BDNA obtained at low surface coverage 2) the two phases obtained at high surface coverage 3) 1D-polymer chains obtained on Au(100) substrates. Reprinted with permission from Held et al. [20] Copyright © 2016 John Wiley & Sons, Inc.

Ag(111) substrate in 2018 [26]. In this new study, products drastically differing from those obtained on Au(111) surfaces were detected, at low and high surface coverage, clearly evidencing the crucial role of the metal on the reaction outcome (See Scheme 3). First of all, reaction selectivity proved to be poor at low surface coverage on Ag(111) substrates. Indeed, the coexistence of four dimerization products i.e. *cis/trans*-enynes, gem-enynes and BDNA issued from Glaser coupling or hydro-alkynylation was simultaneously detected. However, all products did not form in similar yields, the main products being *cis*- and gem-enynes obtained in 67.2 % yield. To a lesser extent, trimers of ENA were also detected, the ratio between ENA dimers and trimers being of 71:29 respectively. Considering that dimers and trimers are formed in the same range of activation temperature, the possibility to reverse the dimer/trimer balance was examined, what is possible by modifying the surface coverage. Indeed, by reducing the molecule concentration on the surface, formation of trimers was greatly favoured, the molecular

tectons benefiting from more space to access to the right orientation (see Fig. 2). A ratio of 21:79 between dimers and trimers could be calculated in these new reaction conditions. Authors also demonstrated trimers not to derive from dimers but to be directly formed by the simultaneous reaction of three ENA units.

Overall, ENA is a versatile building block enabling the formation of dimers by Glaser coupling. Parallel to this expected reactivity on surface, several other reaction pathways have been identified, such as the formation of bis(alkynyl)Au complexes, the cyclotrimerization of alkynes, the hydro-alkynylation reaction or the unprecedented formation of *bis*-acylperoxides. In these different works done on ENA and BDNA done by Fuchs and coworkers, the Glaser couplings have been obtained by means of a thermal activation. In this field, the first example of on-surface Glaser coupling has been reported in 2012 by Barth and coworkers [27], but studies done by other groups have also demonstrated the efficiency of the thermal approach [28]. However,



Scheme 3. The different products obtained upon deposition and annealing ENA on Ag(111) surfaces at low and high surface coverage.

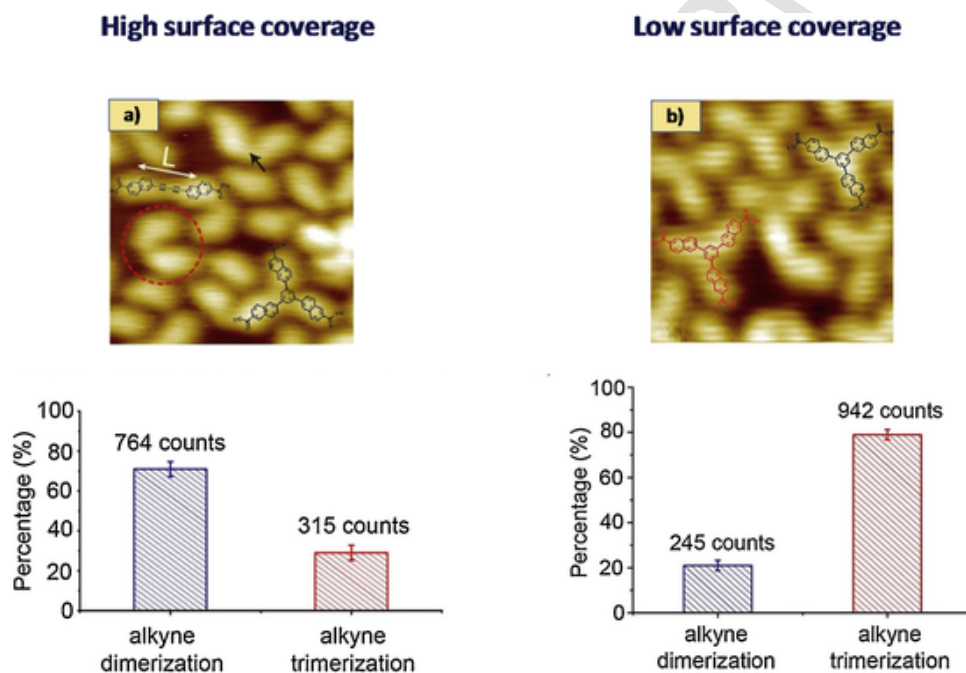


Fig. 2. top : STM images obtained at low surface coverage (1) and high surface coverage (2) bottom : Ratios between dimers and trimers at low and high surface coverage. Reprinted with permission from Klaasen et al. [26] Copyright © 2018 John Wiley & Sons, Inc.

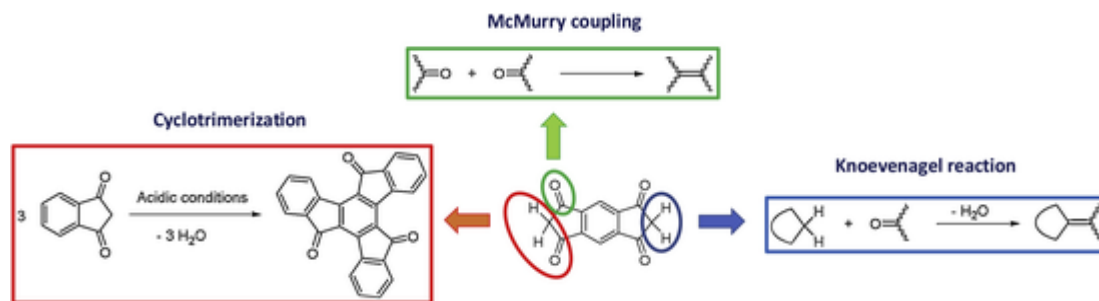
this is not the only way how to initiate the homocoupling of terminal alkynes and the photochemical approach has also been examined to create covalently bound structures on surface [29,30]. Indeed, thermal activation can provide an excessive energy at the origin of the different pathways. In the different works done on ENA, the possibility of initiating different reactivities by thermal activation have been presented by the authors as an advantage. But from another point of view, these different reactions (cyclotrimerization, Glaser coupling, hydroalkynylation) can also be seen as inevitable side-reactions occurring when surface annealing or reactant depositions are triggered at high temperatures so that excessive energies are provided. To avoid the activation of undesired coupling modes at elevated temperatures, introduction of a steric hindrance around the monomer was notably examined as a possible strategy [31]. The thermal activation of alkyne couplings being capable to initiate a large variety of side-reactions, the reaction output of numerous studies cannot be discussed in this review. Indeed, nor the exact chemical structure of the final products could not be identified, nor the co-existence of so much side-products on the surface made these reactions, uncontrolled processes. In this field, the reactivity of

4,4''-diethynyl-1,1':4',1''terphenyl on Ag(111) surfaces can be cited as a relevant example, producing irregular polymeric structures [32].

2. Reactivity of *s*-indacene-1,3,5,7(2*H*,6*H*)-tetrone (INDO4)

In 2017, another building block of interest, namely *s*-indacene-1,3,5,7(2*H*,6*H*)-tetrone (INDO4), was reported as a promising candidate capable to initiate original reactions on surface [33]. From a theoretical point of view, INDO4 is an exciting building block due to the simultaneous presence of numerous reactive functions i.e. four ketone groups and two activated methylene groups, but also by its low molecular weight enabling its deposition to be carried out at low temperature. Considering the large number of reactive functions standing on few atoms, at least, three different reactivities can be anticipated prior to its investigation on surface, based on the chemical transformations known in solution phase chemistry (see Scheme 4).

Here again, the crucial role of the surface topography on the on-surface reactivity was clearly evidenced. Thus, deposition of INDO4 on a Ag(110) surface at the sub-monolayer regime and subsequent annealing of the surface could converted the initial supramolecular phase of IN-



Scheme 4. The different reactivities that can be anticipated by the simultaneous presence of several ketones and methylene groups onto INDO4.

DO4 into a polymeric phase composed of nanoribbons aligned in parallel rows.

As interesting feature, prior to the formation of nanoribbons, the coexistence of two chiral nanodomains in the supramolecular phase could be found. Cavities surrounded by ten molecules aligned $\pm 25^\circ$ with respect to the $[1-10]$ direction and comprising two molecules arranged along the $[001]$ direction were found. The most favorable orientation along the $[001]$ direction was supported by modelisation of the supramolecular phase. Indeed, for the two internal molecules, an adsorption over nine silver atoms could be demonstrated contrarily to the molecules composing the periphery of the cavities, for which an adsorption onto only six silver molecules could be determined (see Fig. 3). Precisely, the most favorable orientation of INDO4 along with the $[001]$ direction also results from the simultaneous adsorption of the four carbonyl groups onto silver atoms, contrarily to the peripheral molecules only adsorbed on the surface by mean of half of the carbonyl functions. Ability of the molecules to find a preferable orientation on the surface was the key element for the surface-governed growth of nanoribbons. Benefiting from this, the covalent coupling between tectons could be thermally activated at 300°C , giving rise to an unprecedented oxidative coupling of unactivated methylene groups and the formation of dimers or trimers aligned in parallel rows. Such a reaction is not achievable in classical chemistry, the homocoupling of indanedione derivatives requiring good leaving groups [34]. Length of the nanoribbons could be drastically elongated by elevating the annealing temperature, providing dimers to pentamers at 350°C . If no significant elongation of the nanoribbons was found at 400°C , loss of the epitaxial conditions of growth were demonstrated at 450°C , with the formation of lateral connections between parallel rows of nanoribbons (See Fig. 4). Interestingly, proofs of a double bond standing between tectons

were evidenced by high-resolution electron energy loss (HREELS) spectroscopy. Indeed, as a first evidence, a vibrational mode corresponding to a $\text{C}=\text{C}$ stretching mode could be identified on the HREELS spectrum. Secondly, the energy gap of INDO4 could not be detected anymore at high energy (2.1 eV), consistent with the formation of a π -conjugated system and a decrease of the HOMO-LUMO gap (with HOMO standing for highest occupied molecular orbital and LUMO for lowest unoccupied molecular orbital).

Interestingly, new coupling modes could be obtained by changing the surface topography [35]. First, contrarily to what was observed on $\text{Ag}(110)$ surface, deprotonation of INDO4 on $\text{Ag}(100)$ substrates was confirmed by HREELS and X-ray photoemission spectroscopy (XPS). Thus, a peak at 2946 cm^{-1} corresponding to the stretching mode of a $\text{C}-\text{H sp}^3$ bond could be detected on the HREELS spectrum of the supramolecular phase of INDO4 deposited at room temperature.

By controlling the temperature, a reaction selectivity could be obtained. Notably, by annealing the surface at 280°C , the formation of dimers 1 issued from a Knoevenagel reaction could be identified as almost the only product coexisting with the unreacted precursor. Conversely, deposition on a $\text{Ag}(100)$ surface held at 350°C could activate simultaneously three coupling modes identified as being the Knoevenagel reaction (1-3), the cyclotrimerization (4) and the oxidative coupling (5) previously detected on $\text{Ag}(110)$ substrates (see Fig. 5). By changing the crystallographic orientation of the surface, a lower activation energy was required to form covalent bonds between molecular tectons on $\text{Ag}(111)$ substrates and obtain a mixture of 1-5. Indeed, presence of the three coupling modes could already be detected at 200°C contrarily to 380°C for $\text{Ag}(110)$ surfaces, evidencing a reduction as high as 180°C of the activation temperature. While coming back to $\text{Ag}(110)$ surfaces, a careful control of the reaction advancement

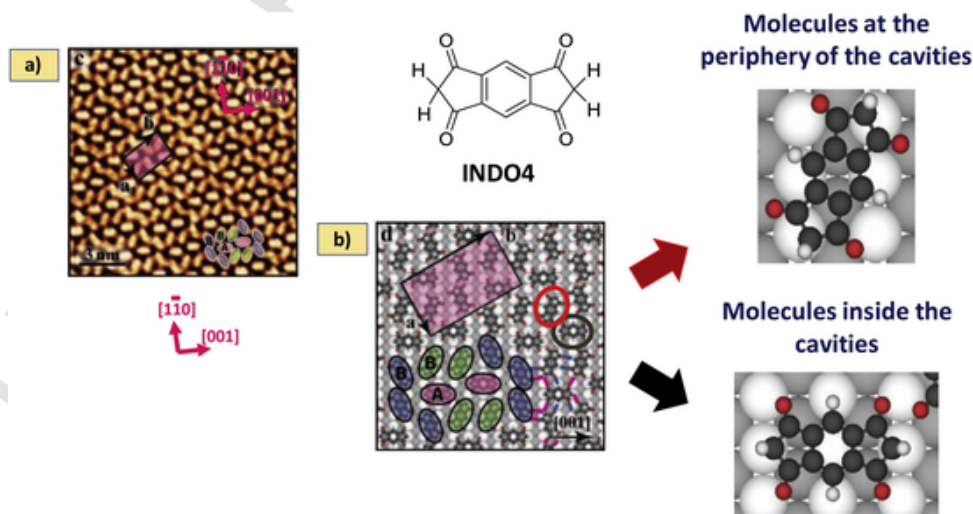


Fig. 3. The supramolecular phase obtained upon deposition of INDO4 on a $\text{Ag}(110)$ surface. a) STM image. b) Tentative model supporting the most favorable orientation along with the $[001]$ direction. Reprinted by permission from Macmillan Publishers Ltd: Nature from [33], copyright 2016.

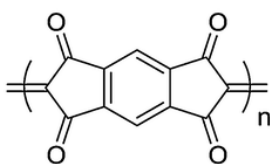
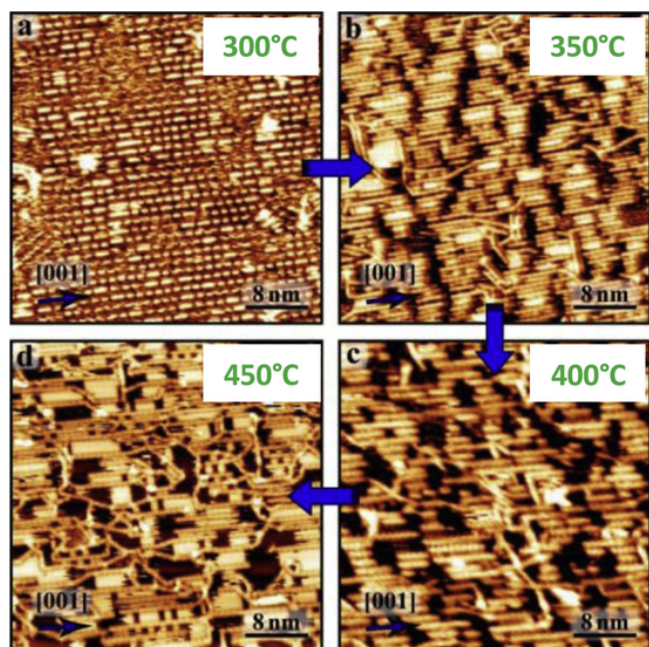


Fig. 4. STM images evidencing the different growth steps of nanoribbons on Ag(110) with the annealing temperature and chemical structure of oligomers obtained by oxidative coupling. Reprinted by permission from Macmillan Publishers Ltd: Nature from [33], copyright 2016.

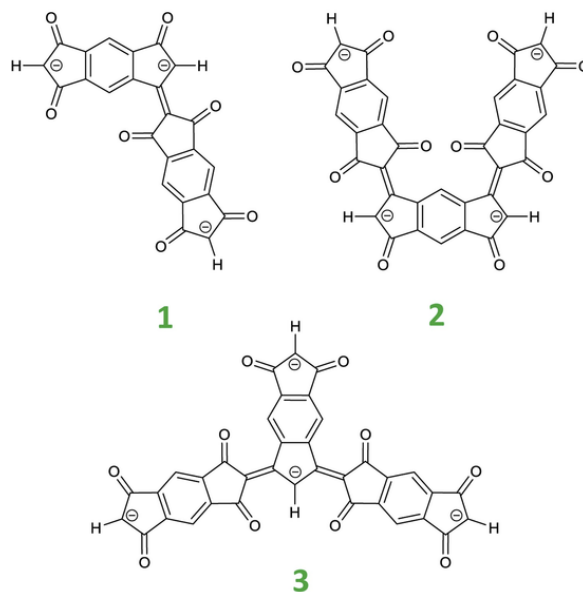
could be obtained, providing dimers at 280 °C, dimers and trimers at 300 °C and finally nanoribbons with size up to 10 nm at 350 °C.

No side reactions were detected on the surface, evidencing a strict reaction selectivity. To the best of our knowledge, INDO4 is the first molecular tecton for which the surface topology can discriminate so efficiently between two well-identified chemical reactions, requiring the precursor to be orientated in different directions (linear alignment of precursors for the oxidative coupling, angle of 120° between precursors for the Knoevenagel reaction). Symmetry of the surface is not the only parameter enabling to discriminate between potential reactions. Indeed, the different experiments done on three different surfaces (Ag(110), Ag(111) and Ag(100)) clearly proved the temperature to be another key-parameter, as exemplified with the careful control of the nanoribbon length on Ag(110) substrates (See Fig. 6).

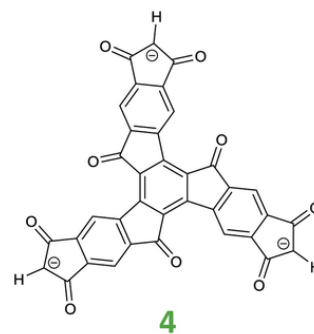
3. Reactivity of 1,3,5-tris(4-acetylphenyl)benzene (TAPB)

The possibility to perfectly direct the formation of π -conjugated films within the two-dimensional constraints of a surface by assembling individual molecules is one of the basic requirements for the bottom-up construction of molecular devices and nanoelectronics [10,36]. If the Ullmann coupling of halogenated precursor molecules has been extensively studied to form π -conjugated networks resembling the graphene sheets [37–41], an appealing and alternative strategy consists in creating additional aromatic rings directly on the surface instead of connecting preformed aryl groups. This strategy was notably applied with the cyclotrimerization of aromatic alkynes producing a benzene ring but this approach remains seldomly investigated [42,43]. An interesting example of cyclotrimerization has been proposed in 2015 with the con-

Knoevenagel reaction



Cyclotrimerization



Oxidative coupling

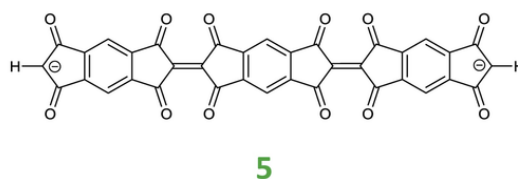


Fig. 5. Chemical structures of compounds 1–5 detected on Ag(111) substrates.

trolled reactivity of 1,3,5-tris(4-acetylphenyl)benzene (TAPB) [44]. Upon thermal activation on the three different surfaces (Ag(111), Au(111) or Cu(111)), two distinct coupling modes were detected, namely, the dimerization of acetyl groups (i.e. a crotonisation reaction) and the cyclotrimerization of TAPB upon thermal activation of the chemical reactions. The reaction output proved to be dependent of both the substrate temperature and the molecular density. The different structures later discussed were directly obtained on the surface and no annealing experiments were carried out to modify the reaction output. In fact, all different attempts of surface annealing by the authors only resulted in the desorption of molecules from the surface, contrarily to what is commonly reported in the literature. If deposition of TAPB at room temperature only furnished a supramolecular phase on all sur-

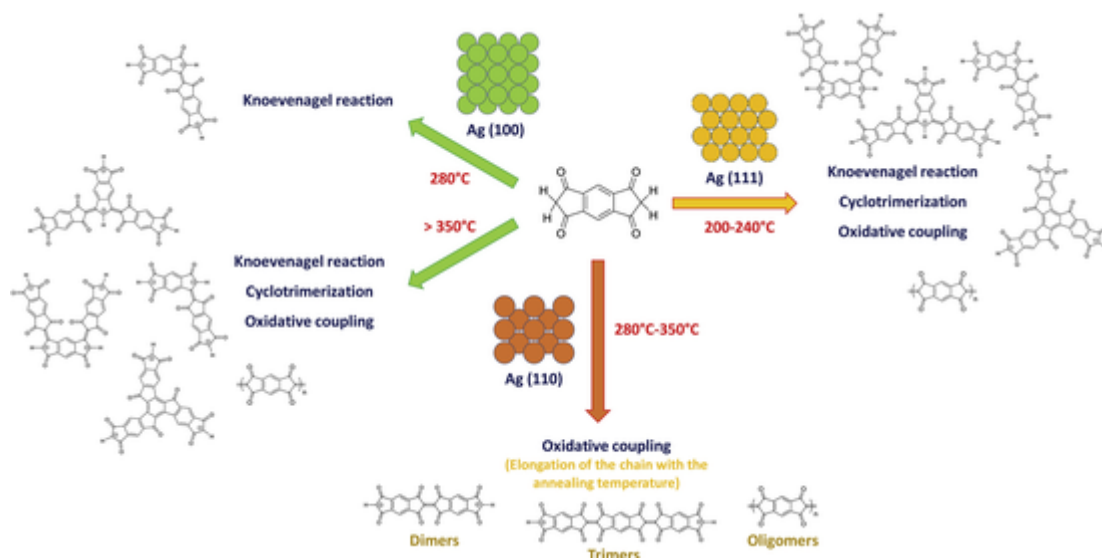


Fig. 6. The different coupling modes observed on Ag surfaces of different topographies.

faces, the chemical reactions (crotonisation, cyclotrimerization) could only be initiated by depositing TAPB on preheated substrates, annealing of the supramolecular phases only resulting in the partial desorption of the molecules. Three main products were detected after evaporation of TAPB on a Ag (111) surface held at 590 K. As shown in the Figs. 7 and 8, a macrocycle and a polycyclic structure resulting from the crotonisation of three or ten TAPB molecular tectons could be detected respectively. Uncyclized motifs resulting from a crotonisation reaction between three TAPB units were also identified. As interesting feature, the cyclotrimerization reaction was only observed for the pyramid-like structures involving ten TAPB units. Indeed, due to the presence of acetyl groups inside the pyramidal structure placed at the appropriate distance, with the right orientation and on the proper surface with a sufficient temperature to trigger the chemical transformation, a cyclotrimerization could occur, converting nine acetyl groups into three benzene rings. In turn, a graphene-like structure with a phenyl ring standing at every vertex and spaced by an aromatic ring was obtained (see Fig. 7). Due to the rigidity of the structure, only 1,3,5-substituted

aromatic rings could be formed by cyclotrimerization, contrarily to what was previously observed for the cyclotrimerization of alkynes for which a mixture of two regioisomers was detected on the surface (1,3,5- and 1,2,4-substituted aromatic rings) [32]. Statistical analysis of the temperature-dependent cyclotrimerization revealed this reaction to be favoured by elevating the surface temperature.

A two-fold enhancement of the number of thermally generated aromatic rings could be detected on the surface by increasing the substrate temperature from 260 °C to 350 °C (See Fig. 9) at identical surface coverage. While getting a deeper insight into the dimerization mechanism, theoretical calculations revealed the dimerization reaction not only to be a cetolisation reaction but to reach the final state of the reaction i.e. the crotonisation state corresponding to the dehydration of the intermediate cetol. Investigations also revealed the dimerization to result from the reaction of a deprotonated molecule with a non-deprotonated one. This mechanism is supported by the easy deprotonation of the functional groups bearing acidic protons, as exemplified with INDO4 on Ag substrates. Importantly, XPS analyses confirmed the inter-

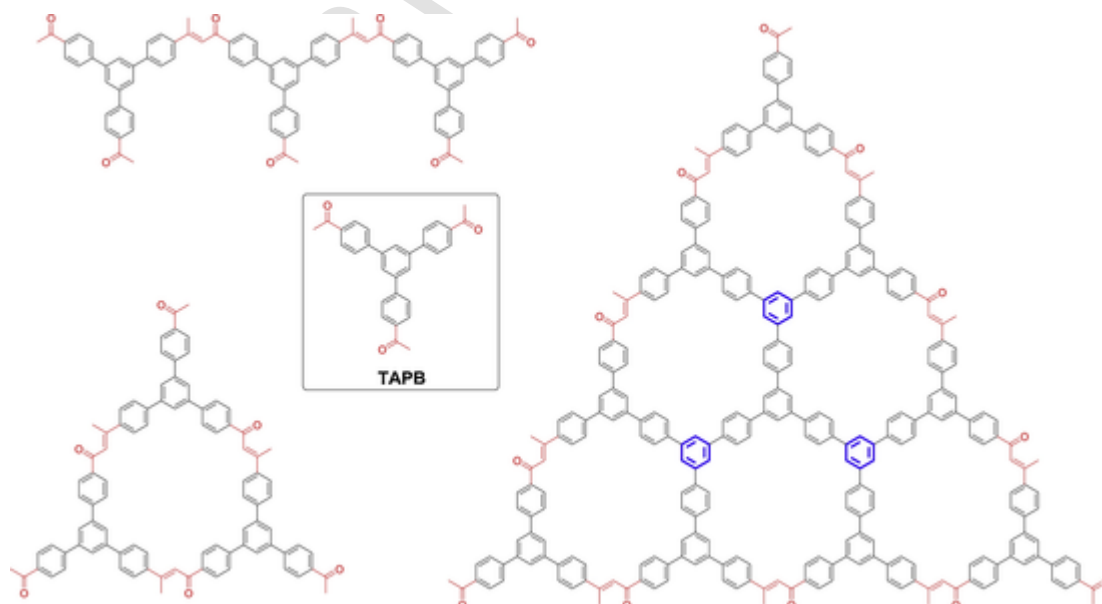


Fig. 7. The main three structures detected on Ag(111) surfaces upon deposition of TAPB on a substrate held at 590 K.

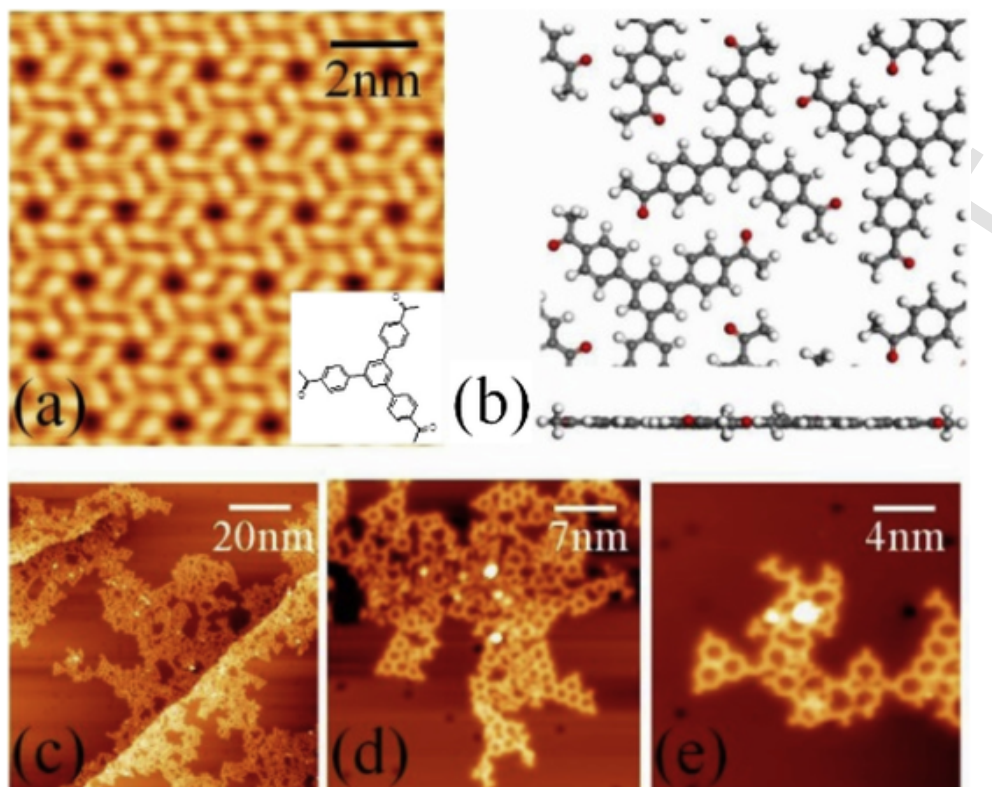


Fig. 8. STM images of TAPB deposited on Ag(111) substrate held at room temperature (a) with the corresponding model (b) and 590 K (c, d and e) at different magnifications. Adapted with permission from Yang et al. [33]. Copyright 2015 American Chemical Society.

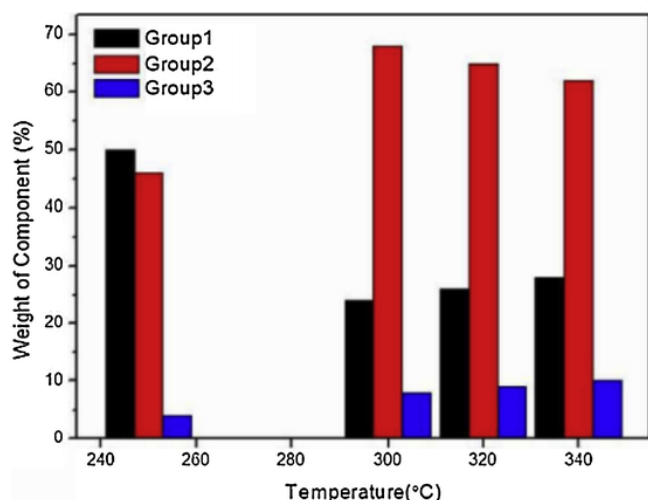


Fig. 9. Statistical analysis of the different motifs detected on Ag(111) surface by varying the substrate temperature. Group 1 (unreacted acetyl group), group 2 (dimers) and group 3 (cyclotrimerized acetyls). Adapted with permission from Yang et al. [33]. Copyright 2015 American Chemical Society.

mediate cetol to be subsequently submitted to a crotonisation reaction by the C—O ratio in the final assembly. In fact, the on-surface crotonisation reaction carried out in two steps resembles that observed in the solution phase chemistry. As other finding, the two reactions (crotonisation, cyclotrimerization) were insensitive to the metal nature, the same products being detected on Au (111), Ag (111) and Cu substrates (111) (see Fig. 10). Finally, by increasing the surface coverage, an extended polymer almost covering the entire surface was found, evidencing the efficiency and the selectivity of the cyclotrimerization reaction (see Fig. 11).

While comparing TAPB with ENA and INDO4, TAPB proves to be the less versatile molecular tecton of the series, only crotonisation and cyclotrimerization reactions being possible with this substitution. However, as observed for ENA, dimerization over trimerization could also be efficiently controlled by mean of the molecular density on surface, enabling to form extended polymers at high surface coverage as shown in the Fig. 11.

4. Conclusions

To conclude, ENA, INDO4 and TAPB constitutes a novel class of molecular tectons in the on-surface synthesis toolbox. Compared to the former generation of molecular precursors, the possibility for tectons to initiate different reaction pathways have introduced additional parameters that can be activated separately such as the temperature, the surface topography and the molecular density. Among the three molecular tectons, ENA has undoubtedly been the most carefully studied. This is also the most versatile building block since at least six different coupling modes have been identified with this molecule, outperforming the two others. Beyond the reactivity of these monomers, the synthetic access and the possibility to prepare derivatives of these structures have also to be considered. From this point of view, INDO4 is the less versatile structure, access to *bis*-indanedione derivatives being clearly a challenge. To illustrate this, only 3 articles report the synthesis of INDO4 [45–47]. If an elongation of the central backbone is considered with the replacement of the phenyl central core by a naphthalene moiety, such a synthesis is only reported once in the literature [48], and even not reported for an anthracene spacer, evidencing the synthetic challenge. Still while considering INDO4, this is also the molecule for which the introduction of peripheral groups is the most difficult, drastically limiting the possibility to bring additional functionalities or properties to the resulting macromolecular structure. No lateral functionalization of INDO4 is reported to date. Considering the infinite of possi-

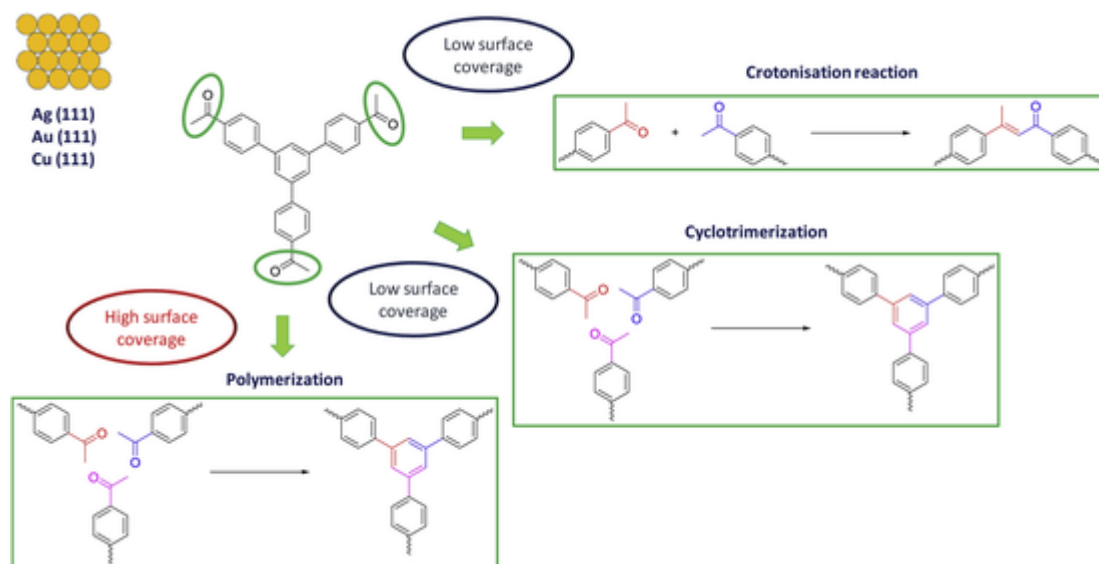


Fig. 10. The different coupling modes of TAPB observed on Ag(111), Au(111) and Cu(111) surfaces.

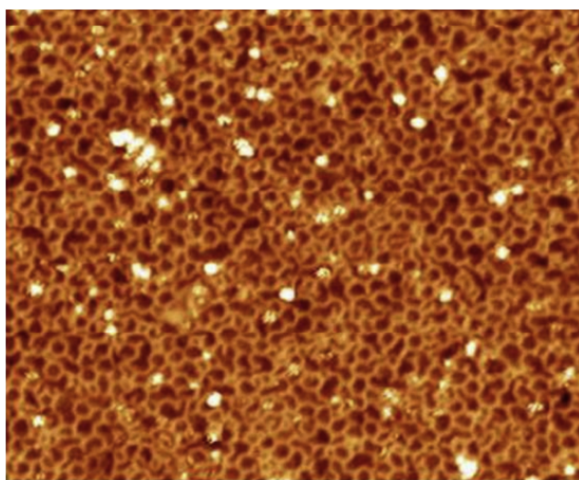


Fig. 11. STM image of TAPB deposited at high surface coverage on Ag(111) substrate. Length of the picture is 50 nm. Adapted with permission from Yang et al. [44] Copyright 2015 American Chemical Society.

ble chemical reactions, the future for this new generation of elemental building blocks is ensured. Besides, all known reactions are not worth of study and only those minimizing the molecularity of the reaction while favoring the liberation of none-corrosive side-products have to be privileged first.

Declaration of Competing Interest

The authors declare no conflict of interest.

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