Perspective

Ullmann-like reactions for the synthesis of complex two-dimensional materials[*]

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Abstract

Engineering two-dimensional materials through surface-confined synthetic techniques is a promising avenue for designing new materials with tailored properties. Developing and understanding reaction mechanisms for surface-confined synthesis of two-dimensional materials requires atomic-level characterization and chemical analysis. Beggan *et al* (2015 *Nanotechnology* **26** 365602) used scanning tunneling microscopy and x-ray photoelectron spectroscopy to elucidate the formation mechanism of surface-confined Ullmann-like coupling of thiophene substituted porphyrins on Ag(111). Upon surface deposition, bromine is dissociated and the porphyrins couple with surface adatoms to create linear strands and hexagonally packed molecules. Annealing the sample results in covalently-bonded networks of thienylporphyrin derivatives. A deeper understanding of surface-confined Ullmann-like coupling has the potential to lead to precision-engineered nano-structures through synthetic techniques.

Keywords: Ullmann coupling, two-dimensional material, porphyrin, STM, XPS

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

Creating and controlling the molecular patterning of conjugated two-dimensional organic materials without manually placing individual molecules is important for their potential integration into self-assembled molecular-based devices because it will allow for engineering of chemical and physical properties as well as solve the problem of how to scale up manufacturing. The 'classic' Ullmann reaction was developed in 1901 and named for Fritz Ullmann. It uses a reductive copper-catalyzed coupling of aryl halides to synthesize symmetric biaryls involving elevated temperatures and a powdered copper catalyst [1]. Ullmann-like reactions are a variant of the 'classic' Ullmann reaction. They too use a metal catalyst to couple aryl halides ultimately resulting in an aryl–aryl bond formation and a metal-halide complex, but use various forms of catalysts and experimental conditions that differ from the original Ullmann reaction [2, 3]. Surface-confined Ullmann-like reactions use a crystalline metal surface as a catalyst to create two-dimensional polymeric networks. The properties and geometries of these networks can be tailored by altering the starting material. Often increasing the complexity of the starting material also increases the complexity of the reaction mechanism and the resulting polymerized two-dimensional network.

Beggan *et al* used a surface-confined Ullmann-like reaction to covalently couple brominated thienyl porphyrins, (5,10,15,20-tetrabromothien-2-ylporphyr-inato)zinc(II) (TBrThP), figure 1(a), on a Ag(111) substrate [4]. Porphyrins have a wide array of applications, and are often found in nature. As an example, hemoglobin, found in red blood cells, has iron-containing porphyrin subunits that bind and transport oxygen. Chorophyl, found in plants, contains manganese-porphyrin complexes that absorb light vital for photosynthesis. The optical properties of porphyrin oligomers can be tuned (e.g. split Soret bands or blue
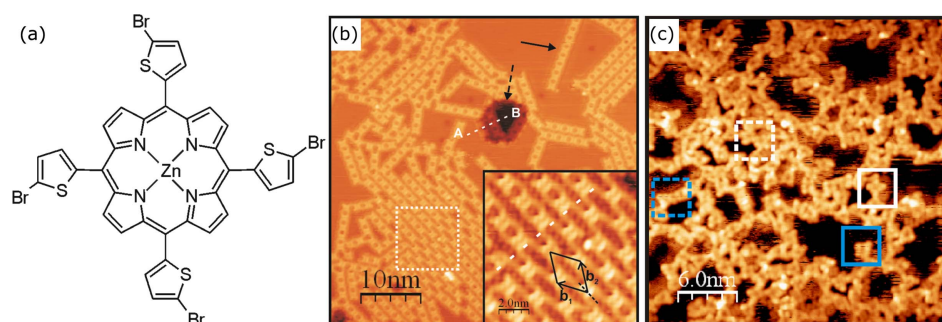
Figure 1. (a) Structure of (5,10,15,20-tetrabromothene-2-ylporphyrinato)zinc(II) (TBrThP). (b) Vapor-deposited TBrThP showing linear and hexagonal packing while coupled to silver adatoms. (c) Annealing at 523 K results in polymeric porphyrins. Reprinted with permission from [4]. Copyright 2015 IOP Publishing.

shifted) by changing the organic linker and number of porphyrins in the oligomer [5]. These light absorbing properties make porphyrins prime candidates for use in dye-sensitized solar cells or light-based therapy techniques [6, 7]. Functional groups can be added at the meso and α carbon positions allowing for engineering of unique porphyrins with specific properties. Use of a flexible porphyrin has allowed Beggan *et al* to create conjugated two-dimensional polymeric networks on the Ag(111) surface.

Conjugated networks of porphyrins show potential for applications that require special light-absorbing and energy-transfer properties [8–10]. Developing and analyzing these materials and chemical processes can be a non-trivial process due to their low-dimensionality and high complexity. A single-atom defect in the material or substrate can change the overall performance of the material. Beggan *et al* used room-temperature ultra-high-vacuum scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) to study the coupled and polymerized porphyrins on Ag(111). STM measures spatially-resolved properties of two-dimensional materials by using tunneling electrons to create a topographical map of atoms and molecules on a conductive surface [2, 3, 11]. STM also gives spatially-resolved information about the electronic properties of the material by imaging filled or empty electronic states [12, 13]. Spatially-resolved local density of states and molecular vibration signatures can be identified using scanning tunneling spectroscopy (STS) and inelastic tunneling spectroscopy (STM–IETS), respectively [12, 14]. Techniques such as XPS, angle-resolved photoemission spectroscopy, and macroscopic transport measurements provide complementary information about the ensemble of molecules on the surface [15]. XPS uses x-rays to scatter core electrons from the sample's surface, the quantity and kinetic energy of these electrons is measured and specific chemical species can then be identified [16]. Beggan *et al* used STM, which provides localized electronic and topographic information, and XPS, which allows for chemical analysis of the monolayer, to tell a more complete story of the chemistry behind this complex surface-confined Ullmann-like reaction.

In order to make a porphyrin amenable to surface-confined Ullmann-like reactions, Beggan *et al* used a porphyrin with four thienyl-halide substituents around the perimeter, figure 1(a). The TBrThP molecules were vapor deposited onto a single crystal Ag(111) surface, which was used as the metal-catalyst. During evaporation and surface adsorption, TBrThP was dehalogenated forming AgBr. The presence of AgBr was supported by XPS results and topographic features seen in the STM image along the perimeter of the linearly arranged TBrThP were attributed to AgBr. After adsorption of TBrThP to the Ag(111) surface, an organometallic intermediate was formed. TBrThP molecules are coupled at the now-vacant Br sites via silver adatoms to create linear and

hexagonally-packed coupled networks, figure 1(b). Submonolayer coverage at room temperature results in mobile TBrThP that couple via surface adatoms forming linear networks. The dominant linear coupling of TBrThP is an interesting result given that TBrThP has four possible coupling sites, one at each corner. These electrophilic networks preferentially align parallel to lower step edges. XPS data supports the preferential adsorption near the electron-rich lower step edges by showing a shift in Br 3p and S 2p core levels to lower binding energy. This shift corresponds to electron donation from TBrThP to the silver surface, indicating electrophilicity of the TBrThP molecule. The abstraction of silver atoms from the surface used to couple TBrThP creates vacancy islands in the substrate. These small vacancy islands are synonymous to step edges, and TBrThP can be seen forming rounded single-strand networks along the lower-step edge.

The deposited TBrThP molecules on Ag(111) were heated to create a covalently-bonded network. Initially heating to 473 K caused desorption of the previously dissociated bromine atoms. This is evidenced by the lack of Br signal in the XPS data and the absence of protrusions that were previously observed around the perimeter of the pre-annealed TBrThP molecules in the STM image. The XPS data suggest that some thienyl groups dissociated from TBrThP as a result of annealing to 523 K. STM images show dot-like features near step edges which are labeled by Beggan *et al* as thienyl group pairs. XPS data show that some thienyl groups remain intact on TBrThP. Predominantly, TBrThP retains 2 or 4 thienyl groups through the annealing process, creating di- and tetra-thienylporphyrin derivatives. The resulting TBrThP derivative radicals covalently coupled and formed irregular conjugated networks on the Ag(111) surface, shown in figure 1(c). Beggan *et al* tentatively suggest that the TBrThP derivatives couple at either the meso-bridge carbons or α carbons of the meso-thienyl groups. The lack of topographical protrusion between molecules in the STM images of the final network suggests that the Ag adatoms are no longer involved in the coupling of the porphyrin derivatives, indicating a complex irregular two-dimensional covalently-bonded network of TBrThP derivatives on the Ag(111) surface.

The work by Beggan *et al* presented the results and details of the reaction mechanism for surface-confined Ullmann-like coupling of thiophene-substituted porphyrins to create coordination networks and conjugated two-dimensional polymeric networks. The ability to control the organization of molecules on a surface by understanding where and how individual molecules react to form a two-dimensional material without placing each molecule individually is an important step in the direction of total bench-top synthesis of molecular-based devices. This work uses a combination of techniques (STM and XPS) to understand the complex process that creates covalently-bonded networks and organometallic intermediates of a surface-confined Ullmann-like coupling reaction.

This work is of high interest as a wide array of halogenated aryl molecules have shown successful surface-confined Ullmann-like coupling to form covalently-bonded two-dimensional networks. These networks include graphene-like nanoribbons [17], porphyrin arrays [3], and complex conjugated-carbon networks [2, 18–23]. Surface-confined Ullmann-like coupling is a promising method for creating unique nanostructures using a bottom-up principle. In order to engineer nanostructures with a particular set of properties, it is imperative to understand their reaction mechanism. Beggan *et al* make a valuable contribution to the discussion concerning the reaction mechanism of surface-assisted reactions, and porphyrins are particularly interesting to polymerize because of their planarity, conformational flexibility, and unique energy-transfer characteristics [10, 24].

Covalently-bonded networks have the capability of transporting charge between molecules and throughout the molecular network. A next step is to properly understand the physics of energy-transfer in the covalently-bonded porphyrin network. The process of energy transfer in a covalent system depends

upon several physical factors such as local and long-range electron distribution, coupling between the host and the foreign molecules, surface characteristics, etc. The effect of electrons is represented by their density of states, which can be calculated by using a quantum mechanical approach such as density functional theory (DFT). Experimentally, STM based spectroscopy, such as STS and STM–IETS, could be used to elucidate transport mechanisms and identify chemical species by probing the local density of states as well as localized vibrational signals from individual molecules. A local DFT calculation would complement spectroscopy experiments by modeling the local density of states for various molecular species. Multi-probe measurements using STM would provide information on longer-range charge and thermal transport properties [25, 26]. These results can be interpreted by using a Green's function (GF) technique that accounts for surface geometry and includes long range effects [27]. The GF, which, by definition, gives the total response of a material to a point probe, can be directly measured by STM for 2D materials [27]. Thus multiprobe STM measurements combined with GF can be a valuable tool for investigating the surface effects on charge and thermal transport.

An integrated approach using a synergistic combination of measurements and modeling of the transport properties of two-dimensional materials will bring these materials one step closer to device incorporation.

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