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Single Layer of Polymeric Fe-Phthalocyanine: An Organometallic Sheet on Metal and Thin Insulating Film

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S *Supporting Information*

ABSTRACT: Supramolecular chemistry on a surface has produced a large variety of atomically controlled systems, but practical applications are seriously restricted by the use of weakly cohesive non-covalent bonds and by the confinement to a metal surface. Here we report on the formation of a well-ordered organometallic sheet consisting of two-dimensional polymeric phthalocyanine. Remarkably, the growth demonstrated on a metal surface can be extended onto a thin insulating film. We thus expect the intrinsic properties to be preserved, and the system should be easily transferable to real devices.

Recent developments in the field of surface-supported supramolecular chemistry have produced a whole range of well-ordered self-assembled organic systems. Intermolecular forces governing self-assembly processes range from van der Waals forces and hydrogen bonds[1,2] to metal−organic coordination[3] or substrate-mediated interactions.[4] In particular, metal-directed assembly can be exploited to engineer highly organized networks, wherein the incorporated transition metal can feature multiple functional properties, depending on the specific coordination environment.[5] Such results bear significant promises for various areas of technological relevance, including catalysis, gas storage, molecular electronics, molecular magnetism, sensor design, optics, and molecular switches and motors.[6−8] Weak, non-covalent interactions are very flexible, and their reversibility during the formation process in the low-dimensional environment of a surface ideally offers the possibility of defect self-healing to produce perfectly ordered networks. Comparatively, the first achievements of covalent polymerization on a surface are either restricted to one-dimensional growth[9,10] or poorly ordered or limited in terms of 2D extension due to the irreversible process of the formation of a covalent bond.[11−15] For such systems, a key point is the possibility of extending polymer conjugation into the second dimension,[16,17] similar to the case of graphene, the simplest carbon-based 2D polymer that possesses extremely high carrier mobility, and that is now seen as a major research field.[18] However, beyond this basic mono-component material, the huge knowledge of organic chemistry awaits for introducing the necessary variety in the structure and properties of such films. The properties of 2D-conjugated polymers have been explored theoretically for more than two decades.[19,20] However, experimental efforts aimed at creating and characterizing such materials are more recent.[17] The challenges include designing properly functionalized monomers that can react in two directions and identifying a suitable template to guide the formation of a continuous 2D network. Because rigid and planar 2D-conjugated polymers are in most cases insoluble, classical solution polymerization and characterization techniques are barely suitable. Atomically flat crystalline surfaces can act as templates to confine polymerization reactions in two dimensions and enable in situ characterization with local probe methods such as scanning tunneling microscopy (STM).

Among technologically relevant molecules for organic electronic devices, the metallophthalocyanines (MPc) are very extensively studied for their chemical and optoelectronic properties.[21] They can be employed as building blocks for a wide range of applications, such as gas sensors, field effect transistors, organic light-emitting diodes, and data storage devices. The polymeric forms of phthalocyanines have been known for a long time,[22−27] but their intermediate (2D) dimensionality makes their synthesis and manipulation delicate. Produced as thin films of mostly undefined structure, they raised a large interest thanks to their good stability in ambient conditions, contrary to phthalocyanine films. They revealed excellent conduction and magnetic properties, however restricted to variable grain boundary conditions. In fact, their intrinsic properties could never be properly studied because they could never be formed in a well-characterized way.

Here we present the formation of a fully 2D-conjugated organometallic sheet. Electron delocalization is provided by a repeating unit based on an Fe-phthalocyanine core;[19] in addition to exquisite conductive and optoelectronic properties inherited from phthalocyanines,[21] the presence of regularly spaced Fe atoms should produce peculiar magnetic properties that are interesting for spin-polarized conduction. We demonstrate that the growth is not limited to the confinement of a metal surface but can be extended onto a thin insulating film. This further achievement represents fundamental advances for exploiting this remarkable material: in this way, a perfectly defined organic metal-on-insulator system is directly built,[28] and the organic layer can probably be relatively easily transferred to various devices and characterization systems by soft lithography techniques.[29]

Our combined approach is based on a metal-directed surface reaction: polymeric arrays were obtained by co-evaporation of Fe and 1,2,4,5-tetracyanobenzene (TCNB, a basic molecular unit commonly used for the synthesis of phthalocyanine derivatives) in ultra-high-vacuum conditions onto atomically clean and well-defined surfaces. TCNB was evaporated from a crucible held at 360 K and Fe using an electron-beam heating evaporator. Varying stoichiometry was obtained by varying the deposition time ratio. The synthetic films formed were characterized by

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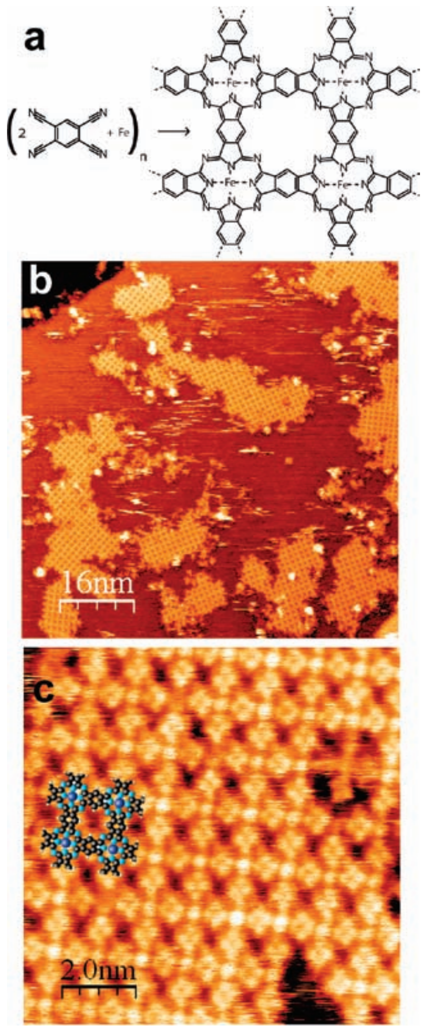

Figure 1. (A) Synthesis reaction scheme of the 2D iron phthalocyanine organometallic polymer (poly-FePc). (B,C) STM images of poly-FePc formed on a Ag(111) surface (square unit cell, 1.15 nm large). Similar results are found on Au(111) (see Supporting Information).

room-temperature STM. Polymer growth is demonstrated on Au(111) and Ag(111), as well as on a thin insulating film of NaCl/Ag(100).

The deposition of TCNB molecules and iron atoms in 2:1 stoichiometry enables the polymerization reaction of Figure 1A. Noticeably, this reaction produces no byproduct, so no contamination is created. Fe atoms were evaporated on a TCNB film, and the reaction took place directly on the surface at room temperature. The as-formed polymeric Fe-phthalocyanine film is presented Figure 1B,C. The film network has a square structure with a measured periodicity of 1.15 ± 0.1 nm in both directions. The relatively small mesh size and the square symmetry reflect the covalent nature of the bonds inside the film, as opposed to longer metal−organic[30,31] or hydrogen[32] bonds that can form between dicyano functional groups. Indeed, hypothetical metal−ligand bonding that would be consistent with the unit size and the stoichiometry would not give the observed pattern and should induce a chiral metal center and clear helicity in the network[31] (see Supporting Information). We modeled the polymer sheet by means of density functional theory calculations (DFT) (see Supporting Information for method) and found a distance of 10.8 Å for the theoretical 2D lattice. Fe atoms appear as bright centers because of their d_{z^2} orbital close to the Fermi level,[33] and the linking organic sections appear as four-fold lobes. On Au(111) and Ag(111), three orientations of the polymer network can be found, reflecting the threefold symmetry of the substrates. Domains of about 10−30 nm are formed, linked by domain boundaries.

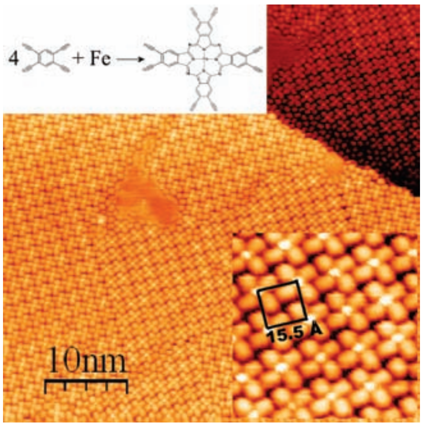

Figure 2. STM image of the 2D self-assembly of in situ synthesized $FePc(CN)_8$ formed on a Au(111) surface by successive deposition of TCNB and Fe atoms in a 4:1 ratio. Inset: reaction scheme.

The control on the stoichiometry of the precursors is crucial for successful reaction: excess of metal or of molecules can hinder the formation of a well-ordered polymer and lead to the formation of disordered undefined phases. Nevertheless, the reaction occurring when depositing TCNB molecules and iron atoms in 4:1 stoichiometry can be also controlled and leads to the formation of individual phthalocyanine molecules, that is, cyano-functionalized Fe-Pc (Fe-2,3,9,10,16,17,23,24-octacyanophthalocyanine, $FePc(CN)_8$). The as-formed molecules then self-assemble in square superlattices with a unit cell size of 1.55 ± 0.1 nm (Figure 2), as usually observed for this class of molecules.[32] Indeed, supramolecular networks formed by $FePc(CN)_8$, $ZnPcCl_8$, or $ZnPcF_8$[34] are of comparable structure and unit cell size (∼1.5 nm). All these networks belong to the same family, as they are built from rigid M-Pc cores connected by hydrogen bonds. X-ray photoemission spectroscopy (XPS) measurements of the Fe $2p_{3/2}$ core-level peak (see Supporting Information) revealed a binding energy at 707 eV that confirmed the formation of organometallic compounds.[35]

Monoatomic (100)-terminated NaCl islands (50−100 nm wide) are formed upon adsorption on Ag(100) at room temperature.[36] We succeeded in growing polymeric phthalocyanine on a such thin insulating film. As molecular species usually adsorb preferentially on the free areas of the metal substrate,[37] it is necessary to saturate the uncovered parts of the surface before growth can be initiated on the insulating islands. Remarkably, polymeric phthalocyanine forms a monodomain phase over NaCl, and the size of the defect-free organometallic sheet is limited to the NaCl island size (Figure 3). The configuration of molecular adsorbates on a thin insulating film was shown to be very close to that of the isolated system.[38] We thus expect the intrinsic properties of the polymeric layer formed on NaCl to be preserved.

In summary, we demonstrated the formation of a polymer network that consists of a polymeric Fe-phthalocyanine single sheet. This π-conjugated system represents a fully delocalized two-dimensional electron system[19] with magnetic metal atoms

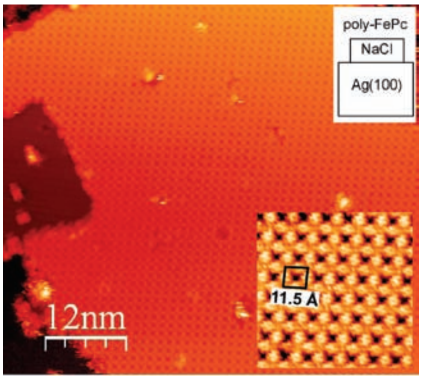

Figure 3. STM image of the 2D Fe-phthalocyanine polymer (poly-FePc) formed on a thin insulating NaCl island deposited on Ag(100) by successive deposition of TCNB and Fe atoms in a 2:1 ratio.

spread regularly in the polymer lattice. In particular, spin-polarized conduction is expected. The growth can be readily extended on a thin insulating film that provides efficient electronic decoupling from the metal substrate. In principle, it should be possible to perform stepwise growth and to create networks of alternating metal centers, e.g., magnetic and non-magnetic, and therefore control the spin density in the film. Individual spins can eventually be adjusted by functionalization and/or modification of the magnetic center,[5] allowing the magnetic properties of the molecular network to be adjusted. Molecular precursors of various size, shape, and functionality could be used,[27] as well as other metals.[24] The flexibility of the synthesis method will thus allow for the creation of a wide range of organometallic polymer films of tunable composition, structure, and properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. STM images of TCNB/Ag(111), poly-FePc/Au(111), and poly-FePc/NaCl/Ag(100); X-ray photoemission data; schematics of hypothetical metal–organic networks; DFT computational details; complete ref 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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