THE JOURNAL OF PHYSICAL CHEMISTRY

Article

Cite This: J. Phys. Chem. C 2019, 123, 20922−20927

pubs.acs.org/JPCC

Solution-Processed Large-Area Ultrathin Films of Metal-Coordinated Electron-Rich Adenine-Based Ligand

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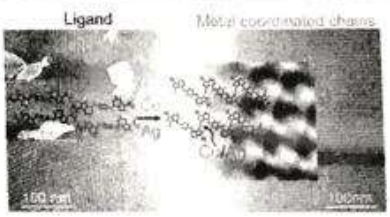
Supporting Information

ABSTRACT: Using a simple solution-based drop-casting method, we demonstrate formation of a large-area (several tens of micrometers) uniform ultrathin film of a metal-coordinated electron-rich ligand based on modified adenine on a highly oriented pyrolytic graphite surface. On the contrary, the ligand alone crystallized into small domains (a few hundreds of nanometers maximum) on the surface. We show that a delicate balance of coordination bonds and weak H-bonding leads to this unusual uniform growth as supported by scanning tunneling microscopy and atomic force microscopy. The mesoscopic uniformity of the film was understood using X-ray photoelectron spectroscopy, while the microscopic pattern of ultrathin films was corroborated with density functional calculations. Two-dimensional films of electron-rich molecules are of importance in thin-film-based electronic applications, and therefore, their economic processing is also of significance.



INTRODUCTION

Semiconducting inorganic/organic molecule based two-dimensional (2D) materials, typically thin films, are of major interest currently in electronic applications.[1−4] Self-assembly and tunability of electronic properties of molecules make them an ideal choice for bottom-up construction of thin films. However, low charge carrier mobilities in molecular thin films, manifested through hopping and tunneling, limit efficiency of devices based on organic semiconducting molecules.[5] One of the ways to improve charge transport in thin films of electron-rich molecules is through doping, comprising predisposed ligand groups, with metal atoms/ions.[6]

Consequently, 2D nanoscale materials with embedded coordinated metal ions/atoms or charge transfer complexes have been successfully prepared for specific applications.[7−9] Charge transport measurements of such metal-doped ultra-high-vacuum[6,10−14] and solution[15]-processed thin films demonstrate that they are suitable for electronic applications. Controlling the microscopic pattern, which in turn tunes the electronic properties, and processing uniform large-area thin films of electron-rich molecules are of importance in thin-film-based electronic applications. Highly selective noncovalent interactions of nucleobases present a distinct advantage in fine-tuning microscopic patterns and have been explored in thin films.[16−25]

In this article, noncovalent interactions of a nucleobase-based electron-rich molecule and metal doping are combined to generate uniform large-area molecular ultrathin films. We demonstrate metal-coordinated molecular chain formation of an electron-rich ligand (**L**, cf. in Figure 1a), composed of two adenine rings linked through a phenyl aromatic linker, and its subsequent assembly to large (several tens of micrometers) 2D films on a highly oriented pyrolytic graphite (HOPG) surface. **L** alone crystallized invoking Watson−Crick hydrogen bonding and C−H···π interactions. The ultrathin film of **L** on the HOPG surface showed small domains (a few hundreds of nanometers maximum) of ligand crystallites. The Cu- and Ag-coordinated ligand 2D films are prepared by a simple solution-based drop-casting method.

EXPERIMENTAL METHODS

The ligand (**L**; N^1,N^4-bis(9-ethyl-9*H*-purin-6-yl)benzene-1,4-diamine) was synthesized, and the details are given in Sections S1 and S2. For preparation of ultrathin films of **L**, 5 μL of ligand in HPLC methanol (concentration ~10^{-5} M) was drop-casted onto a freshly cleaved HOPG surface (ZYB grade from μmasch). The above concentration is critical for the formation of the monolayer and has been optimized after several trials (quality of the film is controlled by AFM images); further increasing the concentration leads to formation of nonuniform thick films. The surface was kept tilted at ~30° for smooth flow of the solution; without tilting, we would obtain nonuniform films and clusters throughout the film. Molecules deposited on HOPG were then kept for drying at ambient conditions (temperature 25 °C and relative humidity ~50%) for complete evaporation of the solvent from the surface and subsequently performing scanning tunneling microscopy (STM) and atomic force microscopy (AFM) experiments. Scotch tape exfoliation was employed to obtain a clean surface of HOPG. **L** was mixed with the metal salt in methanol with a 1:1 volume ratio (concentration ≈ 10^{-5} M) to generate the metal-coordinated ligand layer. $Cu(NO_3)_2$ and $AgNO_3$ were mixed with **L** to

Received: May 23, 2019
Revised: August 4, 2019
Published: August 6, 2019

DOI: 10.1021/acs.jpcc.9b04908
J. Phys. Chem. C 2019, 123, 20922−20927

(11) Self Attested
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