

論文内容の要旨

論文題目 Architectonics of π -Conjugated Low-dimensional Nanomaterials
at Liquid Interfaces

(液相界面を駆使した π 共役低次元ナノ物質の構築)

氏名 松岡 亮太

Introduction

Constructing low-dimensional polymeric nanomaterials with well-defined morphologies is a challenging research target. In this research field, use of a liquid/liquid or gas/liquid interface is an effective approach to organize atomic, ionic, and molecular building blocks in two-dimension. In addition, the interface can serve as a two-dimensional (2D) reaction field for the reactants. Therefore, the liquid interfaces could provide a wide variety of low-dimensional polymeric nanomaterials. Our laboratory has exploited functional coordination 2D polymers (nanosheets) using these interfaces. However, the diversity in chemical bonding or interaction employed in this method has not been extensively explored, resulted in restriction of the accessible structural motifs. The aim of my Ph.D. research is to expand the scope of the liquid interfacial syntheses to versatile low-dimensional nanomaterials. I focus on two distinct structural concepts as typical examples: the van der Waals induced organization of linear coordination polymers and the construction of covalent 2D polymers based on π -conjugated carbon-carbon bond.

Bis(dipyrrinato)metal(II) One-dimensional Coordination Polymers

One-dimensional coordination polymers (1D-CPs) tend either to dissociate in solution or to aggregate randomly, which restricts their practical application. In the master course I have developed synthesis and ordered alignment of a nickelladithiolene 1D-CP at a liquid/liquid interface. Here, I expand the variation of the metal center in bis(dipyrrinato)metal(II) 1D-CPs **M-CP** (**M** = Zn, Cu, and Ni) and investigate the applicability of the Zn-centered polymer to electric conversion systems (Figure 1).

A dichloromethane solution of the dipyrrin ligand was layered with aqueous zinc(II) acetate, giving rise to single crystals of **Zn-CP** suitable for X-ray diffraction analysis. Single crystals of **Cu-CP** and **Ni-CP** were obtained simply by changing the divalent metal ion to Cu^{2+} and Ni^{2+} , respectively, in water. The crystal structures are almost identical to each other for the three metal centers, in which the 1D polymeric chains align in a parallel manner with each other.

The single crystal of **Zn-CP** may be dispersed in an organic solvent upon ultrasonication, which allows us to utilize **Zn-CP** for widespread applications: a conjugate of the coordination polymer and single-walled carbon nanotubes is an active material for thermoelectric conversion devices and the exfoliated fibers deposited on a transparent tin oxide electrode function as a photoelectric conversion system.

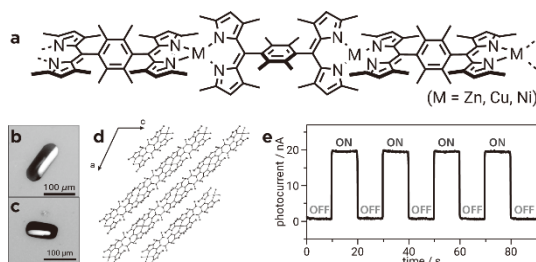


Figure 1. (a) Chemical structure of **M-CP**. (b,c) Single crystal of **Zn-CP** (b) and **Cu-CP** (c). (d) Crystal structure of **Zn-CP**. (e) photoelectric conversion ability of **Zn-CP**.

Graphdiyne nanosheet

Although much efforts have been made to create a wide variety of 2D polymers, those based on carbon-carbon bond formation—the most basic but useful bond in chemistry—are quite scarce, leaving room for further investigation. Here I develop a liquid/liquid or gas/liquid interfacial synthesis of a 2D polymer woven by π -conjugated carbon-carbon bond, graphdiyne (Figure 2).

A liquid/liquid interfacial synthesis using a dichloromethane solution of hexaethynylbenzene (HEB) and an aqueous solution of $\text{Cu}(\text{OAc})_2$ /pyridine catalyst gave a multilayer graphdiyne film at

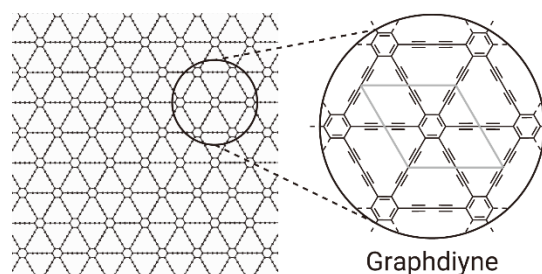


Figure 2. Illustration and chemical structure of graphdiyne.

the interface as a dark brown film at room temperature (Figure 3a). Optical microscopy (OM, Figure 3b) and atomic force microscopy (AFM) visualize its uniform sheet-like morphology with a layered structure. The thickness of the thinner part is 6 nm, corresponding to 17 layers considering the interlayer distance of graphdiyne described in the previous report (0.36 nm, J. Zhou et al. *J. Am. Chem. Soc.* **2015**, *137*, 7596). A selected-area electron diffraction (SAED) image in transmission electron microscopy (TEM) displays a hexagonal pattern, suggesting the crystallinity of the graphdiyne film (Figure 3c). The SAED analysis discloses that the nanosheet has an in-plane periodicity of 0.96 nm and an ABC-type stacking structure.

The multilayer graphdiyne film was also characterized by energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The EDS elemental mapping and XPS reveal that the graphdiyne film is predominantly composed of carbon (Figure 3d–g). A Raman spectrum shows four bands typical of graphdiyne, indicating that the terminal alkyne residues of HEB formed the π -conjugated butadiynyl linkage.

Few-layer graphdiyne was obtained using a modified synthetic procedure, a gas/liquid interfacial synthesis. A very tiny amount of HEB in a mixture of dichloromethane and toluene was gently placed on the surface of an aqueous solution containing the Cu catalyst at room temperature under an inert atmosphere (Figure 4a). The resultant graphdiyne nanosheet floating at the gas/liquid interface was transferred on a substrate using a Langmuir-Schäfer method. Microscopic analyses display that all nanosheet domains have well-defined regular hexagonal shapes, reminiscent of the hexagonal crystal lattice of graphdiyne (Figure 4b). The hexagonal domains have lateral sizes of 1–2 μm and a

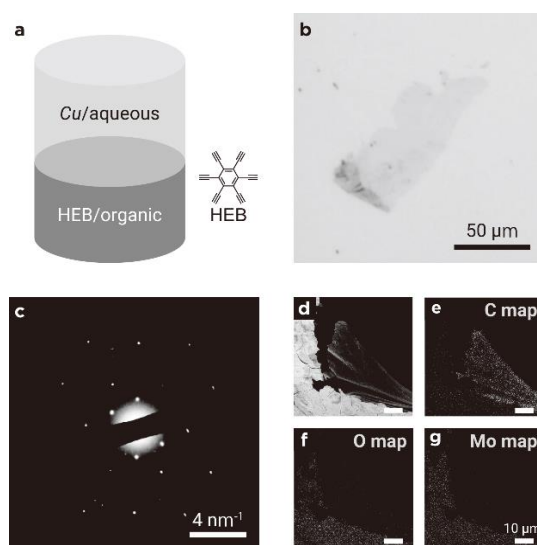


Figure 3. (a) Schematic illustration of the liquid/liquid interfacial synthesis. (b) OM image of multilayer graphdiyne. (c) SAED pattern. (d–g) SEM image on a Mo grid (d) and SEM-EDS mapping for C (e), O (f),

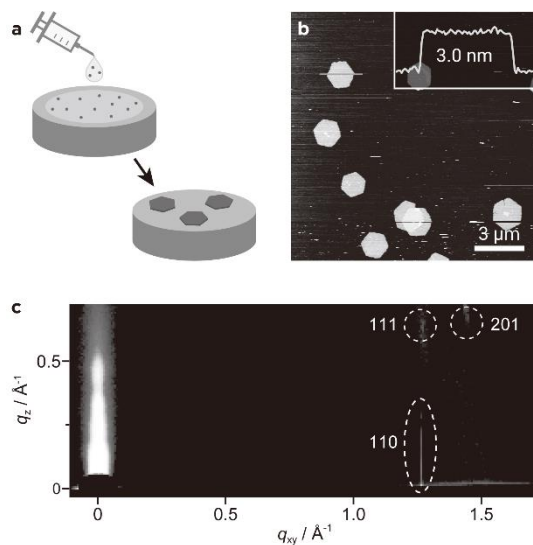


Figure 4. (a) Schematic illustration of the gas/liquid interfacial synthesis. (b) AFM image of few-layer graphdiyne. (c) 2D WAXS pattern.

thickness of 3 nm, corresponding to less than 9 layers of graphdiyne. A two-dimensional wide-angle X-ray scattering (2D WAXS) pattern of the 3-nm-thick graphdiyne features several diffuse spots, deriving a hexagonal lattice with of $a = b = 0.96$ nm and $c = 1.02$ nm (Figure 4c). The interlayer distance calculated from the c value is 0.34 nm, which is consistent with the previous report.

Triphenylene-cored diyne nanosheet

The liquid/liquid interfacial protocol was then applied to the syntheses of another diyne-based nanosheet comprising triphenylene core (Figure 5a). A biphasic system composed of an *o*-dichlorobenzene solution of the hexaethynyltriphenylene (HETP) and an ethylene glycol solution of $[\text{Cu}(\text{OH})\text{TMEDA}]_2\text{Cl}_2$ afforded triphenylene-diyne nanosheet at the interface as a yellow film. The obtained film exhibits a sheet-like structure with a smooth texture in OM and scanning electron microscopy (SEM) (Figure 5b,c). An XPS survey spectrum shows the absence of copper, indicating that no Cu catalyst remains in the film. The existence of sp carbons was confirmed by Raman spectroscopy. Therein, two bands assignable to the vibration of the conjugated diyne linkage (1928 and 2192 cm^{-1}) were observed.

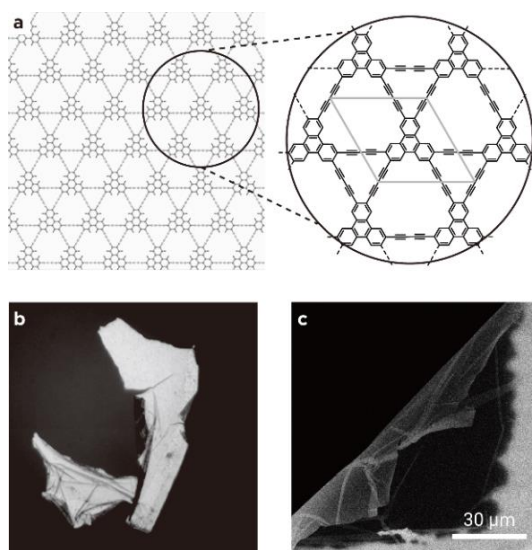


Figure 5. (a) Illustration and chemical structure of triphenylene-diyne nanosheet. (b) OM image. (c) SEM image.

Conclusions

In the series of research, the variation of the dipyrin-metal 1D-CP was expanded, and two covalent 2D polymers woven by π -conjugated carbon-carbon bond were synthesized at liquid/liquid and gas/liquid interfaces. Remarkably, the gas/liquid process yielded graphdiyne single crystals with a regular hexagonal shape as thin as 3 nm. The strategy demonstrated here opened the door to access versatile functional low-dimensional nanomaterials.