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Synthesis and self-assembly of novel porphyrin molecular wires

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Abstract

Sub-micrometer long butadiyne-linked porphyrin wires were synthesized by oxidative coupling of diethynylporphyrin. The porphyrin wires were analyzed by analytical gel permeation chromatography, absorption spectroscopy and matrix-assisted laser desorption/ionization time of flight mass spectroscopy. Observations of the wire were performed by atomic force microscopy. Self-assembled structures of the wires were observed on highly oriented pyrolytic graphite. Self-assembling features of the porphyrin wires depended on the length of the porphyrin wires and the concentration of the depositing solution.

Keywords: Porphyrin wire; π-Conjugated macromolecule; Self-assembled nanostructure

1. Introduction

Long π-conjugated molecular wires have been receiving much attention because they can be used as organic conducting materials and nonlinear optical materials [1–3]. Measurement of the electric conductivity of individual molecules has been focused on establishing a foundation for molecular electronics and has been performed in various ways, e.g., using a nanofabricated electrode [4,5] and by scanning tunneling microscopy (STM) [6]. However, the measurements are still difficult and only a limited number of successful measurements have been reported so far.

Well-ordered structures of organic molecules on devices are required to realize reproducible and reliable functions of the devices. Thus, the fabrication of the molecular nanostructures required for practical molecular electronics entails the challenge of assembling molecules into the required well-ordered structure. The self-assembly technique takes advantage of intermolecular interaction or of interaction between molecules and the substrate surface to achieve a spontaneous organization. Thus, assembling π-conjugated macromolecules on substrate surfaces is one of the key technologies for the fabrication of molecular electronic nanodevices [7].

A number of works concerning the synthesis and self-assembly of π-conjugated molecular wires on substrates have been published [8,9]. Among such wires, porphyrin wires have attracted much attention because of the small HOMO–LUMO gap, high stability, and diversity of the substituents and of the center metal.

We report the synthesis of novel long π-conjugated porphyrin wires and the first demonstration of the self-assembly properties of the sub-micrometer long porphyrin wires on surfaces of highly oriented pyrolytic graphite (HOPG) and other substrates. The oligo-diethynylporphyrin wires were prepared by copper-catalyzed oxidative coupling reaction of diethynylporphyrin, as shown in Scheme 1 [10–13].

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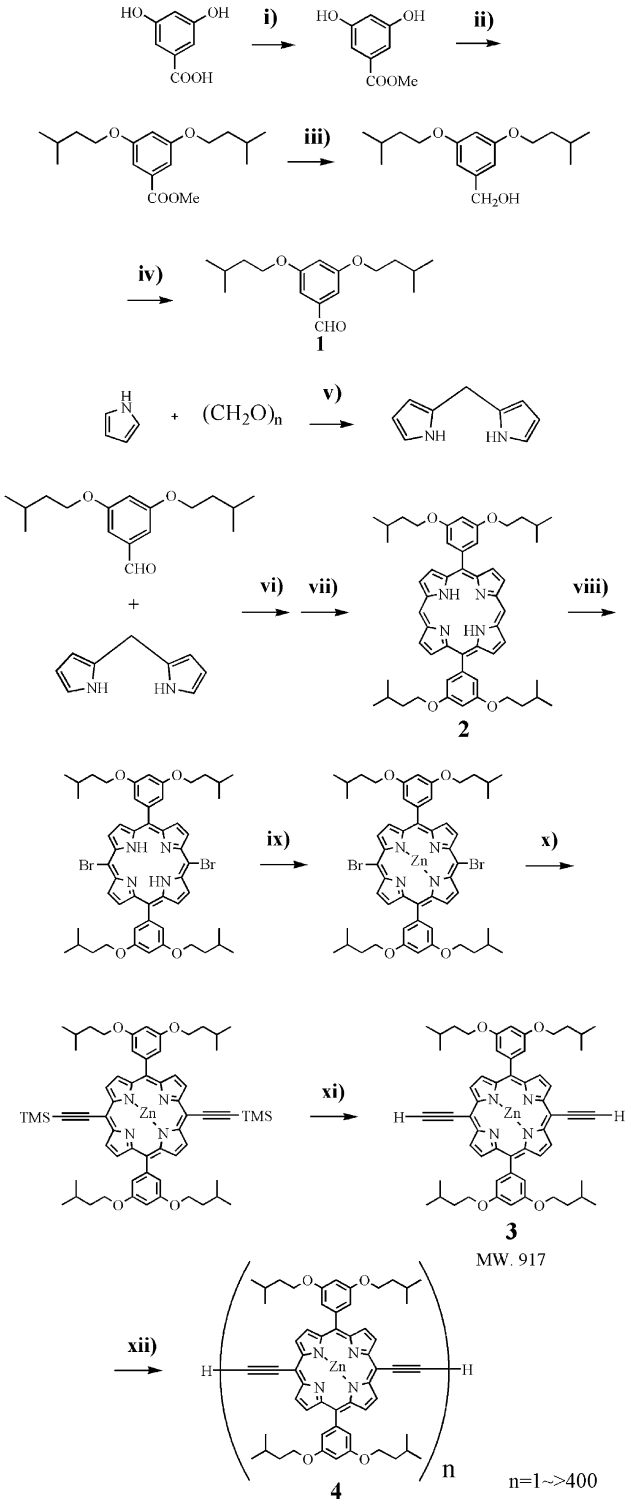

Scheme 1. Synthesis of porphyrin wires. i) TsOH, MeOH, reflux. ii) $C_5H_{11}Br$, K_2CO_3, acetone, reflux. iii) $LiAlH_4$, THF, reflux. iv) MnO_2, toluene, reflux. v) AcOH, MeOH, room temp. vi) TFA, $CHCl_3$. vii) *p*-Chloranil, 333 K. viii) NBS, $CHCl_3$, room temp. ix) $Zn(AcO)_2(2H_2O)$, $CHCl_3$, room temp. x) TMSA, CuI, $Pd(PPh_3)_4$, Et_3N, THF, reflux. xi) TBAF, THF, room temp. xii) CuI, Et_3N, THF, 333 K.

2. Experiment

2.1. Materials

The porphyrin wires were prepared by a modified version of the reported methods, as shown in Scheme 1. 3,5-Bis(3-methylbutoxy)benzaldehyde (**1**) was prepared by MnO_2 oxidation of the corresponding benzylalcohol [14]. 5,15-Bis(3,5-bis(3-methylbutoxy))phenylporphyrin (**2**) was prepared by acid-catalyzed condensation of benzaldehyde **1** with dipyrromethane [15]. Diethynylporphyrin (**3**) was prepared from meso-position-free porphyrin **2** in four steps: bromination [16], metalation with Zn [16], introduction of trimethylsilylacetylene by Sonogashira coupling [17], and deprotection of acetylene units[18]. We prepared oligo-diethynylporphyrin (**4**) by copper-catalyzed oxidative coupling reaction of diethynylporphyrins **3** as follows: Triethylamine (0.5 ml, 5.0 mmol) was added to the THF solution of diethynylporphyrin (**3**) (0.090 g, 98 mmol) and CuI (0.050 g, 0.26 mmol), and the reaction mixture was stirred at 333 K for 24 h in oxygen atmosphere. The resulting solution was purified by gel permeation chromatography (GPC). The solvent was removed under reduced pressure. A dark green powder of the products was obtained (0.078 g, 87%).

The products (reaction mixture hereafter) were purified by preparative scale GPC and analyzed by analytical GPC, absorption spectroscopy, matrix-assisted laser desorption/ionization time of flight mass (MALDI–TOF–MS) and atomic force microscopy (AFM).

2.2. Measurements

MALDI–TOF–MS spectra were obtained using Applied Biosystems Voyager DE-STR with 7,7,8,8-tetracyanoquinodimethane (TCI) as a matrix.

UV–vis absorption spectra were obtained using the Shimadzu UV-3150 spectrometer with pyridine.

Analytical GPC experiments were carried out using Shimadzu LC-6A equipped with the MD-2015 detector (JASCO) using two GPC KF-804L columns (critical molecular weight 400,000 Da, Shodex). The tetrahydrofuran (THF) flow rate in all experiments was 1.0 mL/min.

The samples for AFM measurements were prepared as follows: the porphyrin wires were dissolved in a solvent mixture ($THF/H_2O = 10/1$, v/v), and the solution was cast-deposited onto the substrate surface. We prepared two different concentrations of porphyrin wire solution. One is a solution of porphyrin wires whose absorbance of the soret peak is approximately 0.1 (thin solution). The other is a solution of porphyrin wires whose absorbance of the soret peak is approximately 0.2 (thick solution). These solutions were cast on HOPG, and the solvent evaporated spontaneously. The dried stain on the exterior of the porphyrin wires was observed by AFM. Several substrates such as HOPG, mica, and siliconized SiO_2/Si wafers were used for AFM observation. The siliconized