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Morphology control of one-dimensional supramolecular assemblies by a template polymer

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Abstract

A bottom-up approach to construct nano-size architecture has attracted considerable attention. In this report, we demonstrate the formation of one-dimensional supramolecular assemblies of small organic compounds aligned by a template polymer. Complexation of linear poly(trimethylene iminium) salts and benzoxazylpyridine (bzpybox) ligands yielded linear supramolecular assemblies on the mica surface by electrostataic interaction.

Keywords: Supramolecular assembly; Mica; Pseudorotaxane; Pybox; Secondary ammonium cation

1. Introduction

Bottom-up approaches to construct nano-size architectures have attracted considerable attention. Desirable controls of nano-size objects such as molecules, macromolecules, supramolecular assemblies, nanocrystals and so on have been of much interest toward components for molecular electronics. For example, molecular switch [1], diode [2], transistor [3], memory [4] and wire [5] have been developed until now, and trials to connect and arrange them on substrates such as mica, HOPG and Au are one of the goals of nanotechnology. Formation of supramolecular assembly is one of the most promising routes for construction of complexes of these components by alignment, connection and immobilization of some functional molecules onto substrate [6]. In particular, utility of one-dimensional (1D) supramolecular assemblies by means of the template polymers has been well-documented [7].

We reported previously that 2,6-bis(oxazol-2-yl)pyridine (pybox) and 2,6-bis(benzoxazol-2-yl)pyridine (bzpybox) ligands formed 1:1 complexes with secondary dialkylammonium salts by two complementary hydrogen bonds [8]. The oligomers of the secondary dialkylammonium provided 2:2 or 2:3 complexes by the formation of ladder type supramolecular assemblies of the bis-pybox compounds [9]. More recently, we demonstrated the formation of polymeric complexes of poly(trimethylene iminium) salts (**PTMI**) with bis-bzpybox ligands. They formed extended fibrous structures on mica, and cross-linking of the fibers provided the thermally reversible gels by hydrogen bonds between the bispybox ligands and the secondary ammonium group in the polymer chains [10]. The bidentate molecular structure of the bisbzpybox ligand formed the ladder-type assemblies and acted as a cross-linker between the polymer chains.

In this study, we attempted to immobilize 1D molecular alignment of the bzpybox ligands onto the substrate by using the polymer as the template. Immobilization was performed by electrostatic interaction between the secondary ammonium cations of the polymer and the anionic surface of mica, or Au–S interaction between the thiol groups of the bzpybox ligand and the gold substrate. Thus, we demonstrate preparation of a thiol modified bzpybox ligand and their fixation along the polymer template (**PTMI**).

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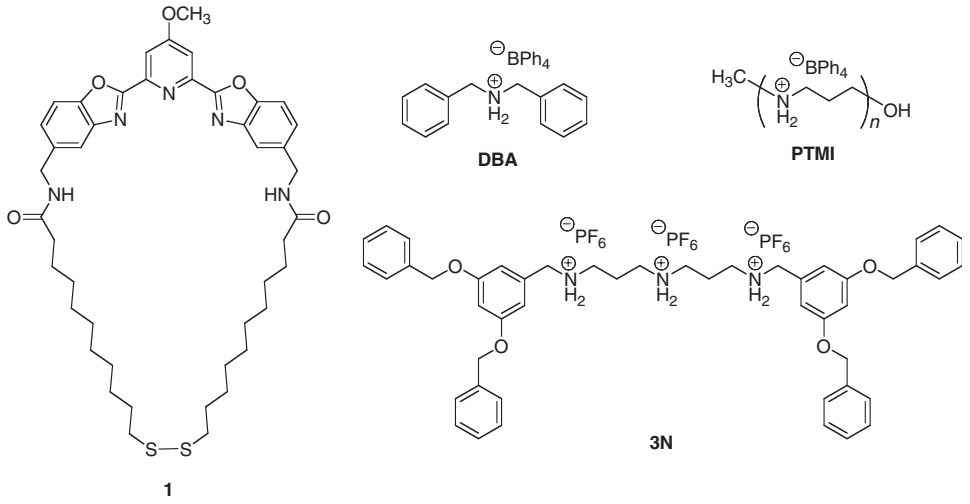

Molecular structure of 1, PTMI, DBA and 3N

2. Experimental section

All starting materials and solvents were purchased form Tokyo Kasei Organic Chemicals or Wako Organic Chemicals and used as supplied. ^{1}H NMR spectra were recorded either on a Bruker AC 250 (250 MHz) or a Bruker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as an internal standard. Mass spectral data were obtained using a Perseptive Voyager RP MALDI-TOF mass spectrometer or JEOL ESI-TOF JMS-T100CS. UV–vis spectra were recorded with a Shimadzu UV-2500 PC. AFM observations were monitored by TopoMetrix TMX 1010.

PTMI was prepared by ring-opening polymerization of 2-methyloxazine according to Ref. [11], and followed by acidic hydrolysis of the amide groups and anion exchange by tetraphenylborate or trifluoromethanesulfonimide. The template secondary ammonium cations are prepared from the primary amines by reductive aminolysis with the corresponding aldehydes.

The thiol-modified bzpybox ligand (**1**) was prepared from chelidamic acid by six steps as shown in Scheme 1. Spectral data of **1:** ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 1.2–1.4(m, 24 H), 1.5–1.7(m, 8 H), 2.25(t, 4 H, $J = 7.1$ Hz), 2.61(t, 4 H, $J = 7.4$ Hz), 4.10(s, 3 H), 4.61(d, 4 H, $J = 5.7$ Hz), 5.83(t, 2 H, $J = 5.6$ Hz), 7.40(d, 2 H, $J = 8.1$ Hz), 7.67(d, 2 H, $J = 8.4$ Hz), 7.76(s, 2 H), 8.01(s, 2 H). ESI-TOF MS: m/e found 800.6 $[M + H^+]$; calcd for $C_{44}H_{57}N_5O_5S_2$ 800.0.

3. Results and discussion

The thiol-modified bzpybox ligand (**1**) was prepared according to Scheme 1. The bzpybox ligand was prepared from chelidamic acid by conventional treatment of 2-aminophenol, followed by bromination of the two methyl groups attached to the benzoxazole rings. Then, amination was achieved by Gabrial synthesis, which was followed by cyclization between 11-dithiodiundecanoyl dichloride and the two amino groups in the high dilution condition to yield the thiol-modified bzpybox ligand (**1**).

First, we investigated complexation of **1** with secondary dialkylammonium cations by ^{1}H NMR and ESI MS spectra. The ^{1}H NMR titration in CD_2Cl_2–CD_3CN 4:1 (v/v) with dibenzylammonium tetraphenylborates (DBA) as a monomeric model provided a change of the chemical shift of the protons as shown in Fig. 1. Addition of the DBA into a solution of **1** illustrated that the resonances of the benzoxazole proton at the 4-position marked with **d** and the proton at the 3-position of the pyridine ring marked with **a** exhibited upfield shifts from 7.75 to 7.64 and from 8.01 to 7.85 ppm, respectively. The proton **c** at the 6-position of the benzoxazole ring showed the downfield shift from 7.42 to 7.46 ppm. These chemical shift changes were quite similar to those observed in the complexation of 2,6-bis(benzoxazol-2-yl) pyridine (bzpybox) ligands reported previously [11]. The binding constants between **1** and DBA were estimated by nonlinear curve fitting in the titration experiment data, and resulted in an averaged binding constant of $K = 2.2 \times 10^3$ (M^{-1}). This value was a tenth magnitude of those of pybox or bzpybox ligand. Moreover, the complexation of **1** with oligomer of the secondary ammonium cations was investigated by ESI-MS in $CHCl_3$–CH_3CN 2:1 (v/v). The salt **3N** was used as oligomers of the secondary ammonium salts, and resulting ESI-MS spectra showed some peaks assigned to the 3:1 complex (m/e of $[13 + 3N + PF6]^{2+}$; found 1642.1, calcd 1642.1, for $C_{180}H_{227}F_6N_{18}O_{19}PS_6^{2+}$). This suggested that **1** can form complexes with secondary ammonium salts which have multiple complexation sites in the same manner of DBA to form pseudorotaxane complexes [12].

The complexation of PTMI and **1** was confirmed by UV–Vis absorption (Fig. 2). However, a trifluoromethanesulfoimide salt of PTMI that has a slightly weaker binding constant to bzpybox ligand was used for UV titration, because the absorption maximum of the