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

Takayuki Suzuki, Yuichi Tateishi, Takahiro Sugimoto, Seiji Shinkai, Kazuki Sada*

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Motoooka 744, Nishi-ku, Fukuoka, 819-0395, Japan

Received 1 April 2006; received in revised form 7 May 2006; accepted 9 August 2006
Available online 3 November 2006

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 electrostatic 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).
2. Experimental section

All starting materials and solvents were purchased from 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 (I) was prepared from chelidamic acid by six steps as shown in Scheme 1. Spectral data of I: $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (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$_{5}$O$_{5}$S$_{2}$ 800.0.

3. Results and discussion

The thiol-modified bzpybox ligand (I) 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 Gabriel 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 (I).

First, we investigated complexation of I with secondary dialkylammonium cations by $^1$H NMR and ESI MS spectra. The $^1$H NMR titration in CD$_2$Cl$_2$–CD$_3$CN 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 I 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 I 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 I with oligomer of the secondary ammonium cations was investigated by ESI-MS in CHCl$_3$–CH$_3$CN 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+PF$_6$]$^{2+}$; found 1642.1, calcd 1642.1, for C$_{180}$H$_{227}$F$_6$N$_{18}$O$_{19}$PS$_6$$^{2+}$). This suggested that I 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 I was confirmed by UV–Vis absorption (Fig. 2). However, a trifluoromethanesulfonimide salt of PTMI that has a slightly weaker binding constant to bzpybox ligand was used for UV titration, because the absorption maximum of the
benzoxazole group is located at a similar wavelength to that of the tetraphenylborate anion. Additions of the solution of PTMI into the solution of 1 induced the red shift of the absorption maximum at 315 nm with an isosbestic point at 334.5 nm, and the intensity slightly decreased and was saturated nearly at 2:1 ratios for monomer units of PTMI to 1. This behavior was similar to those of the ladder-type supramolecular assemblies of the bzpybox ligands with PTMI [10]. The bathochromic shift was attributed to $\pi-\pi$ stacking of the benzoxazole groups aligned along the polymer template, and the thio-modified bypybox 1 formed with 1D molecular assemblies by formation of pseudorotaxane complex in the solution.

Immobilization of the complex of 1 with PTMI onto the substrates was observed by AFM. The bzpybox 1 and PTMI were dissolved in CHCl3–CH3CN 2:1 (v/v), and the mixture was cast onto a fresh mica or gold surface. Following the drying in atmosphere, AFM observation was carried out. As shown in Fig. 3(c), a mixture of 1 and PTMI gave linear molecular assemblies, which were not observed in the sample of 1 (Fig. 3(b)) or PTMI (Fig. 3(a)) only. The averaged length of the linear structures was ca. 80 nm alone corresponding to the polymerization degree of PTMI ($n = 130$). On the other hand, the height profiles of PTMI/1 were in the same magnitude as those of 1. This suggests that the linear assemblies were 1D supramolecular assemblies of 1 aligned by PTMI. The adhesion onto the mica surface was attributed to electrostatic interaction between the positively charged polymer of PTMI and the negatively charged mica surface. On the other hand, trials for immobilization of PTMI/1 onto the gold surface by Au–S interaction failed as shown in Fig. 3(d). Microcrystals of 1 might be deposited on gold surface, and no 1D morphology was observed. Rapid deposition of
the thiol-modified bzpybox 1 by Au–S interaction and incompatibility between the hydrophobic gold surface and the highly charged polymer of PTMI caused the change of supramolecular assemblies of the complex and made fixation of 1 aligned along the 1D template polymer difficult.

4. Conclusion

In conclusion, we demonstrated formation of the 1D molecular complexes of the bzpybox ligands with PTMI. PTMI acts as the template for 1D arrays of 1 by hydrogen bonds between the bzpybox group and the secondary ammonium cation. On mica surface, the complex forms linear supramolecular assemblies deposited by electrostatic interaction between the template and the surface. Molecular design of the template polymer enables us to draw a wide variety of supramolecular architectures on the mica surface toward molecular devices. For example, observation for complex of 1 with branching PTMI is under current investigation.

Acknowledgment

We acknowledge the financial support for Grant-in-Aid (B) and (S) from the Ministry of Education, Culture, Science, Sports and Technology of Japan. T.S. and S. S. acknowledge financial support by a Grant-in-Aid for the 21st Century COE Program “Functional Innovation of Molecular Informatics” from the Ministry of Education, Culture, Science, Sports and Technology of Japan.

References

[1] (a) A.R. Pease, J.O. Jeppesen, J.F. Stoddart, Y. Luo, C.P. Collier, J.R. Heath, Acc. Chem. Res. 34 (2001) 433;
(b) A.P. de Silva, H.Q.N. Gunaratne, C.P. McCoy, J. Am. Chem. Soc. 119 (1997) 7891;
(c) A.P. de Silva, I.M. Dixon, H.Q.N. Gunaratne, T. Gunnlaugsson, P.R.S. Maxwell, T.E. Rice, Issue Series Title: J. Am. Chem. Soc. 121 (1999) 1393;
d) D. Gosztola, M.P. Niemczyk, M.R. Wasielewski, Issue Series Title: J. Am. Chem. Soc. 120 (1998) 5118.
[2] (a) J. Chen, M.A. Reed, A.M. Rawlett, J.M. Tour, Science 286 (1999) 1550;
(b) P.A. Derosa, S. Guda, J.M. Seminario, Issue Series Title: J. Am. Chem. Soc. 123 (2001) 16440;
(c) M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H.B. Weber, M. Mayor, Proc. Natl. Acad. Sci. 102 (2005) 8815.
[3] (a) W. Liang, M.P. Shores, M. Bockrath, H. Park, Nature 417 (2002) 725;
(b) J. Park, A.N. Pasupathy, J.I. Goldsmith, C. Chang, Y. Yaish, J.R. Petta, M. Rinkoski, J.P. Sethna, H.D. Abruna, P.L. McEuen, D.C. Ralph, Nature 417 (2002) 722;
(c) M.R. Diehl, D.W. Steuerman, H.-R. Tseng, S.A. Vignon, A. Star, P.C. Celestre, J.F. Stoddart, J.R. Heath, Issue Series Title: Chem. Phys. 4 (2003) 1335.
[4] (a) C.P. Collier, G. Mattersteig, E.W. Wong, Y. Luo, K. Beverly, J. Sampali, F.M. Raymo, J.F. Stoddart, J.R. Heath, Science 289 (2000) 1172;
(b) A. Sugasaki, M. Ikeda, M. Takeuchi, S. Shinkai, J. Chem. Soc., Perkin Trans. 1 (1999) 3259;
(c) T. Mizuno, M. Takeuchi, I. Hamachi, S. Shinkai, Chem. Commun. (1997) 1793;
d) Y. Furusho, T. Kimura, M. Mizuno, T. Aida, Issue Series Title: J. Am. Chem. Soc. 119 (1997) 5267;
(e) L.J. Prins, F.D. Jong, P. Timmerman, D.N. Reinhoudt, Nature 408 (2000) 181.
[5] (a) H. Engelkamp, C.F. van Nostrum, S.J. Pickers, J.R.M. Nolte, Science 284 (1999) 785;
(b) S. Tamaru, M. Takeuchi, M. Sano, S. Shinkai, Angew. Chem. Int. Ed. 41 (2002) 853;
(c) S. Kawano, S. Tamaru, N. Fujita, S. Shinkai, Chem. Eur. J. 10 (2004) 343;
(d) D.R. Bowler, J. Phys.: Condens. Mater 16 (2004) 721.
[6] (a) G. Cooke, Issue Series Title: Angew. Chem. Int. Ed. 42 (2003) 4860;
(b) N. Weber, C. Hamann, J.-M. Kern, J.-P. Sauvage, Issue Series Title: Inorg. Chem. 42 (2003) 6782;
(c) J.I. Garcia-Lopez, S. Zapotoczny, P. Timmerman, F.C.J.M. van Veggel, G.J. Vancso, M. Crego-Calama, D.N. Reinhoudt, Chem. Commun. (2003) 352;
(d) A. Ikeda, T. Hatano, S. Shinkai, T. Akiyama, S. Yamada, J. Am. Chem. Soc. 123 (2001) 4855.
[7] (a) T. Kanno, H. Tanaka, N. Miyoshi, T. Kawai, Jpn. J. Appl. Phys. 39 (2000) 1269;
(b) T. Shimomura, T. Akai, T. Abe, K. Ito, J. Phys. Chem. 116 (2002) 1753.
[8] (a) K. Sada, T. Sugimoto, T. Tani, T. Yi, S. Shinkai, H. Maeda, N. Tohmori, M. Miyata, Chem. Lett. 32 (2004) 758;
(b) T. Suzuki, S. Shinkai, K. Sada, Y. Tateishi, T. Tani, S. Shinkai, Tetrahedron Lett. 45 (2005) 8161.
[9] T. Sugimoto, K. Sada, S. Sakamoto, K. Yamaguchi, S. Shinkai, Chem. Commun. (2004) 1226.
[10] T. Suzuki, S. Shinkai, K. Sada, Adv. Mater. 18 (2006) 1043.
[11] (a) T. Saegusa, H. Ikeda, H. Fujii, Macromolecules 6 (1973) 315.
[12] (a) Recent examples see T. Takata, Polym. J. 38 (2006) 1;
(b) N. Kihara, K. Hino, T. Takata, Macromolecules 38 (2005) 223;
(c) T. Takata, N. Kihara, Y. Furusho, Adv. Polym. Sci. 171 (2004) 1;
(d) M. Okada, Y. Takashima, A. Harada, Macromolecules 37 (2004) 7075;
e) M. Okada, A. Harada, Org. Lett. 6 (2004) 361.