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Author(s)	梁, 昊赫
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Description	Supervisor:由井伸彦, マテリアルサイエンス科学研究科, 博士

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ABSTRACT

This dissertation reports the establishment of polyrotaxane loop-immobilized surface as a design of dynamic surface and its surface properties for biomaterials. The dynamism of proteins and lipids in cells, such as the lateral diffusion of plasma proteins and the fluidity of lipid membranes, is directly related to signal transduction and amplification across the plasma membrane in the course of intracellular metabolism. It has been suggested that modulation of cellular and tissue metabolisms via their dynamic interfaces with biomaterials is one of the goals in development of advanced medicine and therapy. In the last few decades, Yui group have proposed the importance of molecular mobility in the design of biomaterials, and demonstrated that polyrotaxanes are a promising tool in performing a variety of biomedical functions. A polyrotaxane is a class of molecular assemblies in which cyclic compounds are threaded onto a linear polymeric chain capped with bulky end-groups at both terminals. One can easily imagine that the cyclic compounds can be freely sliding and rotating along the chain in a polyrotaxane architecture if non-covalent interactions among the components are eliminated. Herein, this dissertation was written about how to immobilize the polyrotaxane onto the substrate and the effect of bio-inertness.

Chapter 2 reports about **Immobilization of Polyrotaxane on a Solid Substrate as the Design of Dynamic Surface**. For the immobilization of the polyrotaxane onto the substrate, sulfur-containing groups were introduced at both terminals, which form Au-S bonds. The polyrotaxane was prepared by using PEG-bisamine as a guest polymer chain, α-CD as a host molecule, and tyrosine derivative as a cap molecule. The formation of the polyrotaxane was characterized by GPC and ^{1}H NMR measurements.

For the immobilization of the polyrotaxane onto the substrate in a looped mode, the concentration in 1N NaOH aq. was controlled. The polyrotaxane-immobilized substrate was characterized by IR-RAS, QCM, and XPS measurements. First of all, the immobilization of the polyrotaxane onto the substrate was investigated by IR-RAS and wide-scanned XPS measurements. The immobilized amount was investigated by QCM measurement. Furthermore, the extent of the polyrotaxane immobilized in a looped mode was measured by QCM using colloidal Ag, which forms Ag-S bond at the free thiol group existing on the polyrotaxane grafted onto the substrate. This result was supported by high-resolution XPS measurement, which investigated the area of S2p such as bonded and unbonded sulfur.

Chapter 3 reports **Preparation of Polyrotaxane Loop Surface using Self-Assembled Monolayer Formation**. For the formation of polyrotaxane loop onto an Au substrate, SAM-forming triethyleneglycol dodecanethiolate groups were conjugated at the both terminals of the cap molecule. The formation of the polyrotaxane was characterized by ^{1}H NMR measurement. In chapter 3, two important points have to be considered for bio-inert properties; one is effectively polyrotaxane loop onto an Au substrate and another is effectively to modify the bare surface except the immobilized polyrotaxne. Herein, the SAM concept was introduced for the purpose. The polyrotaxane loop-immobilized substrate was prepared by two steps; the first is to immobilize the polyrotaxane onto the substrate by controlling the concentration in 1N NaOH aq. and the second is to immobilize SAM-forming triethyleneglycol dodecanethiolate group. As the result, the polyrotaxane loop was effectively formed by using the two steps, which was confirmed by QCM measurement upon the conjugation of colloidal Ag. Furthermore, polyrotaxane graft, PEG loop, and PEG graft surfaces as the references were prepared by using the two-step protocols with controlling the

immersion time.

Chapter 4 reports **Loop Formation of Methylated α-Cyclodextrin and Poly(Ethylene Glycol) Based Polyrotaxane on Surfaces Effectively Eliminating Fibrinogen Adsorption**. From the measurement of dynamic contact angles, it was confirmed polyrotaxane loop and graft surfaces exhibited much interesting wettability than PEG loop and graft; higher advancing and lower receding contact angles. Polyrotaxane loop surface on a SAM-modified substrate significantly eliminated the non-specific adsorption of fibrinogen, which can trigger platelet adhesion and the subsequent events leading to blood clotting.

***Key words*: water-soluble polyrotaxane, immobilization, Au substrate, QCM, XPS, dynamic contact angle, SPR**