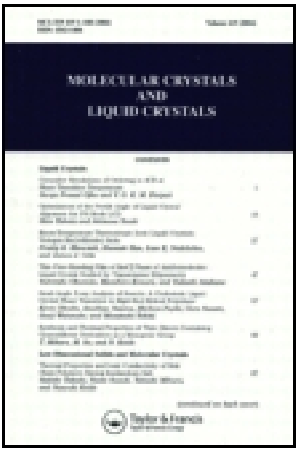

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Hybridization of Polynucleotides Using Self-Assembled Monolayer Containing Pyrenyl Groups

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Hybridization of Polynucleotides Using Self-Assembled Monolayer Containing Pyrenyl Groups

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To realize an efficient hybridization of polynucleotides, self-assembled monolayer (SAM) containing pyrene groups was prepared on a gold substrate because pyrene molecules have an affinity for nucleic acid bases through van der Waals interaction. The SAM was prepared from 11-(1-pyrene)-1-undeacathiol and 11-mercapto-1-undecanol mixed solution. The mixed SAM gave an efficient hybridization of polyadenylic acid and polyuridylic acid observed by surface plasmon resonance.

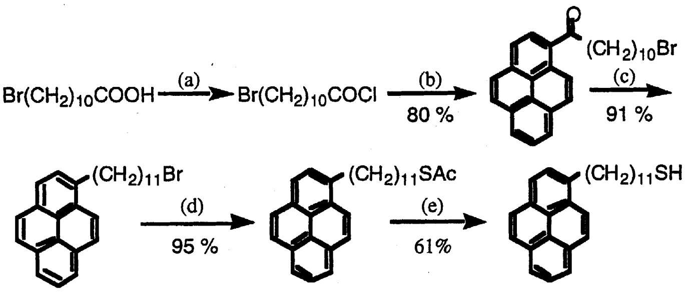
Key Words: Polynucleotides; Hybridization; Self-assembled monolayer; Pyrenyl group; Surface plasmon resonance

INTRODUCTION

Immobilization of single stranded polynucleotides onto a solid surface without denaturation is important for an efficient hybridization of DNA, leading to the determination of the sequence.[1,2] On the other hand thiol or disulfide derivatives can form a closely-packed monolayer on a gold substrate, called a self-assembled monolayer (SAM), when the metal substrate is immersed in the thiol or disulfide derivative solution.[3,4] We have already established the immobilization method of polynucleotides utilizing the SAM containing anthryl groups and confirmed an efficient hybridization.[5] Here, pyrene derivative containing thiol group was synthesized and used to immobilize single - stranded polynucleotides on a solid surface and to realize hybridization of polynucleotides on the surface. (Figure 1) Immobilization and hybridization of polynucleotides were monitored in situ by surface plasmon resonance (SPR).

EXPERIMENTS

The schematic procedure for the synthesis of 11-(1-pyrenyl)-1-undecathiol (Py-C11-SH) is shown in Scheme 1. The structure of Py-C11-SH was identified by H^1-NMR and FT-IR.[6] As a mixture, 11-mercopto-1-undecanol (HO-C11-SH) was used. The SAM was prepared by immersing a gold substrate into a 1 mM ethanol solution of Py-C11-SH and/or HO-C11-SH for 24 hours at room temperature. The polyadenylic acid (poly(A)) and polyuridylic acid (poly(U)) used in this study, which were both from SIGMA, were dissolved in 0.2 M NaCl solutions at a concentration of 0.05 g/l.



SCHEME1 Reagents and conditions: (a) $SOCl_2$, benzene, reflux, 1h. (b) pyrene, $AlCl_3$, CH_2Cl_2, 0°C, 3h. (c) Trifluoroacetatic acid, Et_3SiH, CCl_4, r.t., 5days. (d) Thioacetic acid potassium salt, THF, ethanol, reflux, 9h. (e) NaOH, butanol, reflux, 3h.

RESULTS AND DISCUSSION

In SPR measurements, the adsorption process occurring at the solid-liquid interface can be followed in-situ by selecting an appropriate angle of incidence θ and monitoring the reflected intensity as a function of time.[7] The adsorption of poly(A) and poly(U) onto the SAMs prepared using the solution of Py-C11-SH and HO-C11-SH was shown in figure 2. Poly (A) was adsorbed onto the SAMs containing pyrene groups, while little amount of poly(A) was adsorbed onto the SAM prepared using a pure HO-C11-SH solution. This means the poly(A) can interact with pyrene in the SAM through van der Waals interaction. The amount of adsorbed poly(A) onto the mixed SAM was more than that onto Py-C11-SH SAM. The reason why the number of adsorbed poly(A) decreased was that pyrene groups were closely packed on the SAM, then nucleic acid bases can not interact with the pyrenyl groups. In the case of the SAM prepared using a pure Py-C11-SH solution, poly(A) was adsorbed onto the SAM, while only a small amount of poly(U) was adsorbed onto the poly(A)-precovered SAM. In the case

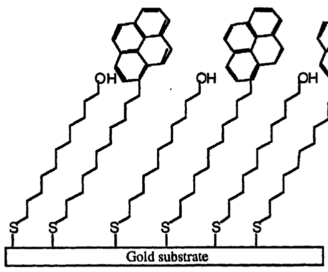


FIGURE 1 Schematic illustration for SAM prepared using a Py-C11-SH and HO-C11-SH mixed solution on a gold substrate.

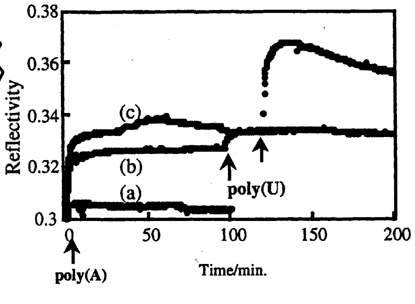


FIGURE 2 Adsorption behavior of poly(A) and poly(U) onto SAMs prepared from:(a) HO-C11-SH, (b) HO-C11-SH and Py-C11-SI mixture, (c) Py-C11-SH solutions .

of SAM prepared from the equimolar mixed solution of Py-C11-SH and HO-C11-SH, subsequently added poly(U) could be adsorbed onto the poly(A)-precovered SAM. This result indicates that hybridization of poly(A) and poly(U) was realized on the SAM. In the case of SAM prepared using a pure Py-C11-SH solution, poly(A) was so tightly adsorbed on the SAM and the poly(A) could not interact with poly(U) on the SAM.

CONCLUSION

We succeeded in preparing SAM containing pyrenyl groups and realizing hybridization of poly(A) and poly(U) using the SAM. By mixing Py-C11-SH and HO-C11-SH, the efficiency of the hybridization was increased. By introducing this functionalized SAM, a new DNA monolayer has been realized without flattening and denaturation, because the interaction between the intercalator and DNA is due to the van der Waals interaction.

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