Photochemical Synthesis of R-shaped DNA via 5-Cyanovinyldeoxyuridin

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ABSTRACT

We now report template-directed photoligation using ODN containing α²U and β²U at both terminal ends. By using this method, we performed template-directed photoligation in two positions at the middle of DNA and synthesized R-shaped DNA as novel structure. The isolated R-shaped DNA was characterized by MALDI-TOF MS and enzymatic digestion.

INTRODUCTION

DNA has been shown to be one of the most exciting molecules available for use in nanotechnology. Because of the programmable base-pairing system and selectivity, DNA is widely utilized for arranging organic and inorganic molecules, proteins, and nanoparticles. The past 10 years have seen remarkable success in the construction of DNA nanoarchitectures. For example, one- and two-dimensional DNA lattices and dendrimerlike DNA have been constructed from a rich set of branched DNA. Synthetic non-nucleic acid molecules serve as linkers or branched point of DNA nanoarchitecture. According to this approach, a chemically synthesized core tethered by two or more DNA oligomers may contribute additional structural or chemical properties while maintaining its capabilities for Watson-Crick base pairing, thus enabling specific supramolecular self-assembly. There are also few reports on the photochemical introduction of a branched segment by crosslinking to the complementary strand using photosensitizer-containing oligodeoxynucleotides (ODN). We previously reported a highly efficient and reversible template-directed DNA photoligation of 5-vinyldeoxyuridine derivative containing ODN at the 5’ end with ODN containing thymine at the 3’ end. In addition, we have recently disclosed an efficient template-directed photoligation ODN using 5-cyanovinyl-1’,α-2’-deoxyuridin (α²U)-containing ODN at the 3’ end with ODN containing thymine at the 5’ end. By using these methods, we have succeeded in the synthesis of complex DNA structures such as branched-DNA, end-capped-DNA or padlocked plasmid DNA at desired site. These unique structure can be a powerful tool for easy and accurate DNA handling, leading to the development of DNA nanoarchitecture as represented by various crossover DNA motifs.

We now report the template-directed photoligation by the use of α²U- and β²U-containing ODN and demonstrated a synthesis of R-shaped DNA as a unique structure like a lariat DNA.

RESULTS AND DISCUSSION

The synthesis of the photoreactive nucleosides and the corresponding phosphoramidite building block of α²U and 5-cyanovinyl-1’,β-2’-deoxyuridin (β²U) as well as the synthesis of corresponding oligodeoxynucleotide followed standard routes in DNA-chemistry (Figure 1). α²U was synthesized from Hoffer’s chlorosugar; the scheme was reported previously. The synthesis of β²U is shown in supporting information. The modified ODN containing α²U and β²U, 5’-d(β²UGCAGTCGCAα²Up)3’ (ODN 1), was synthesized using 3’-phosphate CPG. After reverse phase HPLC purification, the modified ODN 5’-d(β²UGCAGTCGCAα²Up)3’ (ODN 1) was characterized by MALDI-TOF MS (calc. 3189.06 for [M-H], found 3189.06). The ODNs used in this study are summarized in Table 1.

![Figure 1. Structures of α-5-cyanovinyldeoxyuridine (α²U) and β-5-cyanovinyldeoxyuridine (β²U).](https://example.com/figure1)

<table>
<thead>
<tr>
<th>ODN</th>
<th>Sequences</th>
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<tbody>
<tr>
<td>ODN 1</td>
<td>5’-d(β²UGCAGTCGCAα²Up)-3’</td>
</tr>
<tr>
<td>ODN 2</td>
<td>5’-d(GAGACGTGAT)d(A)y(TGGCAATCG)-3’</td>
</tr>
<tr>
<td>ODN 3</td>
<td>5’-d(CGTACTIONGAGCAGCAGCAGCGATCGATCGATCGATCG-3’</td>
</tr>
</tbody>
</table>

We determined the feasibility of the template-directed photoligation via ODN containing α²U and β²U at the
DNA nanodevices as part of the nanostructures. These unique structures are a powerful tool for easy and accurate DNA handling, leading to the development of DNA nanorchitecture as represented by various crossover DNA motifs. Additionally, these methods may be used for the in vitro DNA processing for any DNA such as genome DNA and plasmid DNA.

REFERENCES


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