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Invited review

Photochemically relevant DNA-based molecular systems enabling chemical and signal transductions and their analytical applications

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ABSTRACT

In biology, DNA is the central molecule that stores the genetic information. DNA also has attractive physicochemical features for use as materials in molecular assemblies. DNA is chemically stable and can be prepared in nearly any length and sequence by chemical and enzymatic syntheses. Auxiliary functional groups can be built into the backbone as amidite reagents using automated DNA synthesizers. In addition, we can choose an appropriate method from abundant chemistries for post-modifications. The structures of DNA complexes can be rationally designed by bottom-up self-assembly. Therefore, functional groups can be positioned on the DNA scaffold in distinct distance and spatial arrangements.

In the last decade, a number of DNA-based allosteric molecular systems have been reported. Some of the systems function as signal transducers, amplifiers, and chemical catalysts. These systems are rather exciting as fundamental achievements of the studies for nanomachines or nanodevices. They should also be useful as robust molecular sensors for sensitive bioassays. In this review, we will cover the photochemically relevant DNA-based molecular systems. They are classified into three groups: (i) DNA-templated molecular/ion assemblies; (ii) DNA-directed complexation; and (iii) chemical transformations accelerated on DNA.

Contents

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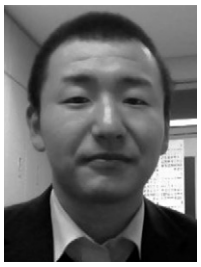

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1. Introduction

All living organisms share nucleic acid as common genetic material. The nucleobase sequence of DNA stores and imparts genetic instructions, whereas RNA functions as a messenger and regulator of gene expression. The elucidation of the 3D structure of DNA in 1953 by Watson and Crick provided a significant boost to biological research [1]. Intensive studies over nearly six decades have made revolutionary progress in our understanding of biology, and the impetus of further characterization of biological processes continues unabated. With the efforts of genome sequencing [2,3], significant advances in biology have contributed not only to medicinal and diagnostic sciences but also to other fields including archaeology, evolution, parentage testing, and forensic science [4].

Besides the significance of DNA in biological processes, scientists have found various uses for DNA within completely non-biological context [5,6]. Some of the fundamental techniques developed in molecular biology including DNA chemical synthesis and PCR (polymerase chain reaction) enable researchers to use DNA as chemical components in elaborate DNA nanostructures. A deep understanding of the mechanical and chemical properties of DNA and the physical chemistry associated with DNA hybridization were also essential for developing the research field of DNA nanostructures. DNA origami is one of the typical achievements in this field of research [7,8]. As the independent line in the nucleic acids sciences, functional nucleic acids such as aptamers, ribozymes, and other allosteric DNA molecular systems have been developed in 1990s [9,10]. These techniques added dynamic or allosteric features to DNA nanostructures such that these compounds could be used as switchable molecular systems that are applicable as molecular sensing devices. That is, the functional nucleic acids merged biology with DNA nanotechnology to realize DNA nanomachines or nanodevices [9–12]. The molecular beacon (MB) is one of the most successful nanodevices [13,14]. The design concept of the MB is flexible. It is based on a reversible structural transformation in response to a specific target DNA. The MB is recognized as an important motif of nanodevices and is commonly used as a part of more complex molecular systems.

Controlled alignment of auxiliary functional groups (i.e., non-biological molecules with fluorescent character, electronic properties, or specific chemical activity) on biomolecular scaffolds such as nucleic acids and proteins has been investigated for the design of catalysts for specific reactions or as probes that response to specific chemical or physical stimuli. Recently, several DNA-directed molecular assemblies with cooperatively developed functions have been reported [15–17]. DNA is chemically stable and the techniques used to synthesize DNA (chemical and enzymatic) have matured. Therefore, various chemical groups can be covalently introduced into DNA to obtain DNA conjugates with desired artificial functions. The programmability and switchable (reversible) nature of specific DNA structures as scaffolds enable us to form supramolecular complexes in which several functional groups or split functions are brought together with defined distances and spatial orientations. If reversible binary motion of the functional groups on DNA is controlled by specific stimuli the DNA assemblies act as allosteric nanodevices for chemical or signal transformation processes (Fig. 1).

Among such DNA-based functional molecular assemblies, we have focused on systems that accelerate specific chemical transformations that are promoted by light and that produce optically or electrically active products. Each specific structure of DNA such as hairpins, duplexes, triplexes, and quadruplexes require particular conditions (e.g., pH, ionic strength, temperature etc.) to maintain their native structure in aqueous solution. Therefore, built-in and designed reactions on these DNA-based assemblies should involve reactions that proceed efficiently in aqueous media under mild conditions. Several bioorthogonal chemical reactions have been recently developed [18]. That has stimulated and aided the progress of allosteric chemical systems on biomolecules.

A lot of the excellent works using DNA probes labeled by Q-dots (quantum dots) and Au nanoparticles have been the subjects of some precedent reviews. The DNA probing based on the simple FRET (Förster resonance energy transfer) between the organic dyes aligned on DNA were not covered in this review. The photochemically relevant DNA-based molecular systems selected here are categorized into three groups: (i) DNA-templated assemblies via hydrophobic and/or electrostatic interactions; (ii) DNA-directed metal complexation; and (iii) chemical transformation promoted on specific DNA molecules.

2. DNA as a nanomaterials template

Recently, DNA has received significant attention as a template for constructing several nanomaterials, because of its inherent structural order and polyelectrolyte character. In addition, the programmability of DNA in its lengths and sequences affords the production of well-defined 1D nanostructures.