Preface

Nucleic acids have structurally evolved over billions of years to effectively store and transfer genetic information. One of the simplest, elegant, and information-rich nucleic acid structures is the double-stranded DNA (dsDNA). The remarkable specificity of molecular recognition between complementary nucleobases and structural robustness have made DNA an attractive biomolecule for molecular programming that involve information coding and decoding purposes. Two complementary single-stranded DNA (ssDNA) molecules spontaneously hybridize through canonical Watson–Crick (WC) base pairing to form a right-handed DNA double helix (dsDNA), which is ~2 nm thick and exhibits a persistence length of ~50 nm, making it a perfect nanomaterial at the molecular level. The disruptive thinking of Nadrian Seeman in the 1980s led to the utilization of DNA as a nanomolecular building block (analogy to a brick) to construct emergent molecular systems and nanomaterial objects of varied size and shape. This bottom-up approach to construct nanoscale architecture with DNA marked the beginning of a new and exciting field of research, namely DNA nanotechnology, which is contributing significantly to the broad area of nanoscience and nanotechnology. DNA nanotechnology was further advanced by the concept of DNA origami, which offers complexity and diversity, developed by Paul Rothemund and others. DNA nanotechnology has been an active and celebrated area of research. It has evolved significantly from its original form, although it relies on complex computer-based design, programming, and the use of very long DNA sequences, while concerns related to the ease of adoptability, reproducibility, and cost-effectiveness for practically utility need to be addressed. On the other hand, templated or co-assembly of functional molecules or any designed structural units and short DNA/RNA oligonucleotides (dB_n, where B = nucleobase, n < 40–50, which corresponds to persistence length of DNA) offers simple and cost-effective means to construct hybrid DNA nanosystems and architectures with novel properties and guaranteed applications.

Such a solution-processible technology based on controlled molecular assembly of functional organic molecules and nucleic acids is an emerging area of research, and its full potential needs to be harnessed through dedicated research efforts. Specifically, covalent and noncovalent co-assembly of functional units and short oligonucleotides constitutes a minimalistic approach and an attractive alternative to construct functional nanoarchitectures. The "molecular architectonics" (Avinash and Govindaraju, 2018) of designer small molecules and short DNA sequences through complementary binding interaction is certain to generate well-defined functional nanoarchitectures with realistic applications in areas ranging from biology to materials science and is termed "DNA nanoarchitectonics." The concept of nanoarchitectonics has been introduced and pioneered by Masakazu Aono and Katsuhiko Ariga, NIMS, Japan.

Contextually, in line with the proverb famously mentioned by Niels Bohr, "It is very hard to predict, especially about the future," it is impossible to predict the future, especially of DNA, which evolved through rigorous selection of nature and synthetic chemistry innovations. We have to agree on one thing that there is a bright future ahead for DNA, either as a genetic material or as a construction material! All we need to do is simplify the concepts and working models to maximize the applications of DNA/RNA in all spheres of scientific and technological disciplines. Synthetic organic chemistry plays a key role in accessing novel functional molecules, modified ssDNA/RNA and their conjugates, and incorporation of desired chromophores. The DNA/RNA nanoarchitectonics is highly dependent on the conventional or unconventional complementary base pairing, and finding suitable molecular partners is quite challenging but certainly not impossible. For instance, generating 3D objects using templated assemblies of small molecules and DNA with precise control of molecular organization on the nano-, meso-, and macroscale without any dispersion is another challenging task. Structural and functional switching at molecular and material levels, with reasonable control on the time and response to the chosen stimulus, is the key to success. The future directions for the field also include programming of templated assemblies of synthetic

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small molecules and DNA to control biological events. The fields of molecular architectonics and DNA nanoarchitectonics involving small functional molecules and short oligonucleotides are expected to grow quickly and find a wide range of applications in chemistry, biology, engineering, (bio)materials, and biomedicine.

In this book, novel approaches adapted by leading researchers in different parts of the world to create functional nucleic acid molecular systems and nanoarchitectures is covered under the topic "Templated DNA Nanotechnology: Functional DNA Nanoarchitectonics," a major subtopic envisaged under the broad subject area of DNA nanotechnology. Individual chapters contributed by active practitioners provide the readers with fundamental and advanced knowledge emanated from their own work and others in the subject area. Each chapter provides plenty of illustrations, historical perspectives, case studies and practical examples, critical discussions, and future prospects. This book can serve as a practical handbook or advanced graduate textbook for students and advanced-level researchers.

Hans-Achim Wagenknecht and Robert Hofsäß discuss covalent DNA-chromophore architectures, photoinduced processes within the chromophore stacks, and their use as artificial light-harvesting systems in the first chapter. This thorough and detailed discussion of a variety of covalent DNA conjugates and their applications sets the necessary foundation for the book. In Chapter 2, Prolay Das and Seema Singh describe pre- and postsynthetic modifications of DNA, programmed DNA–synthetic molecule hybrids, characterization, and their nanostructures, properties, and applications. From our group, we describe a novel concept of mutually templated functional molecule–DNA architectures supported by the canonical and noncanonical hydrogen-bonding interactions of nucleobases, and their functional properties and applications in Chapter 3. The use of functional molecules and their assemblies as a template for ssDNA to generate hybrid DNA ensembles with emergent properties guarantees efficient and cost-effective practical applications across disciplines. Reji Varghese et al. provide a detailed description of design, challenging synthesis, self-assembly of DNA amphiphiles, and the resultant DNA nanostructure as soft nanoscaffolds for various applications in Chapter 4. The self-assembly of DNA amphiphiles leads to nanoarchitectures with a dense display of ssDNA on the surface, which is extremely hard to achieve using the principles of structural DNA nanotechnology and DNA origami approaches. In Chapter 5, Philippe Barthélémy et al. present hybrid amphiphiles featuring DNA nucleobase–lipid conjugates and their interesting self-assembly properties to design a new generation of functional and responsive materials. The authors discuss the behaviors of these systems at the nanometer scale, translation of the nanosystems into advanced soft materials at the macroscopic level, and new opportunities that these soft materials bring to the field of biomedicine. In Chapter 6, Mahesh Hariharan et al. introduce the reader to thorough and eloquent details of photoexcited state processes in templated DNA–chromophore assemblies. The advanced photophysical and photofunctional properties help in understanding the mechanism of light-induced lesions and electronic communication between the chromophores and DNA nucleobases, which in turn help in deciphering the oxidative damage repair pathways in the biological systems and the development of light-harvesting and optoelectronic devices, presented in this and other chapters. Mitsunobu Nakamura et al. deal with another interesting concept of metal-supported construction of a templated assembly of multichromophore arrays and DNA in Chapter 7. In addition to providing a general introduction to the concept of metal-supported functional chromophore–DNA assemblies, the authors describe multichromophore arrays supported on a Au substrate and their photocurrent responses due to electron transfer through the π-stacked array. Chapter 8 by Alberto Bianco et al. discusses the merger of DNA nanotechnology and carbon nanotechnology, which is very exciting and futuristic. Interactions of DNA and RNA with carbon materials and the utility of their complexes in gene and cancer therapy are described. A description of noncovalent and covalent conjugates of single- and double-stranded DNA/RNA with carbon nanotubes (CNTs), graphene oxide (GO), and their novel functional properties is particularly noteworthy. Joshy Joseph et al. present functional nanoarchitectures fabricated through the self-assembly of fullerene derivatives and DNA, with special focus on optoelectronic and biomedical applications, in Chapter 9. The authors introduce the reader to different modes of DNA–fullerene interactions, fullerene-induced DNA condensation, and higher-order nanostructures, including fullerene cluster–assisted DNA assemblies. In Chapter 10, Ashwani Sharma et al. discuss nucleic acid–based molecular devices and biosensors. A major portion of this chapter deals with aptamers and their application in designing biosensors for detection, imaging, diagnostics, and therapeutics. The final chapter (Chapter 11) discusses the utilization of highly predictable molecular recognition of nucleobases, unique characteristics of flexible ssDNA, rigid dsDNA, and associated reversible conformational transformations of canonical and noncanonical DNA structures for developing nanoswitches and devices with numerous applications, including sensors of ions, pH, and biomolecules, as well as to develop diagnostic and therapeutic tools. Overall, all the chapters are well organized, interconnected, and futuristic in presentation.

I thank all the authors for their excellent contributions to this unique book through plenty of case studies, attractive illustrations, thought-provoking concepts, and future outlook. Finally, I take this opportunity to thank Prof. C. N. R. Rao, the messiah of materials science and nanotechnology, for his constant support and encouragement and dedicate this book to his 85th birthday.

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