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Invited Review

Use of biomolecular scaffolds for assembling multistep light harvesting and energy transfer devices

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ABSTRACT

The development of biologically templated artificial light harvesting antennae and energy transfer devices is a highly active research area with exceptional challenges. Natural energy harvesting complexes have exquisite spectrally- and spatially-tuned systems with high redundancy to maximize their ability to gather, channel, and distribute electromagnetic radiation. Attempting to mimic these highly efficient systems requires at the very least (sub)nanoscale precision in the positioning of light sensitive molecules, the latter of which must also possess carefully selected photophysical properties; in essence, these two fundamental properties must be exploited in a synergistic manner. First, the scaffold must be highly organized, ideally with multiple symmetrical components that are spatially arranged with nanoscale accuracy. Second, the structure must be amenable to chemical modification in order to be (bio)functionalized with the desired light sensitive moieties which have expanded greatly to now include organic dyes, metal chelates, fluorescent proteins, dye-doped and noble metal nanoparticles, photoactive polymers, along with semiconductor quantum dots amongst others. Several families of biological scaffolding molecules offer strong potential to meet these stringent requirements. Recent advances in bionanotechnology have provided the ability to assemble diverse naturally derived scaffolds along with manipulating their properties and this is allowing us to understand the capabilities and limitations of such artificial light-harvesting antennae and devices. The range of scaffold or template materials that have been used varies from highly symmetrical virus capsids to self-assembled biomaterials including nucleic acids and small peptides as well as a range of hybrid inorganic–biological systems. This review surveys the burgeoning field of artificial light-harvesting and energy transfer complexes that utilize biological scaffolds from the perspective of what each has to offer for optimized energy transfer. We highlight each biological scaffold with prominent examples from the literature and discuss some of the benefits and liabilities of each approach. Cumulatively, the available data suggest that DNA is the most versatile biological material currently available, though it has challenges including precise dye placement and subsequent dye performance. We conclude by providing a perspective on how this field will progress in both the short and long term, with a focus on the transition to applications and devices.

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Christopher M. Spillmann graduated with a Bachelor of Arts (Physics) from the College of Wooster in 1997 and a Ph.D. in Biophysics from the University of Rochester in 2004. His graduate studies focused on the mechanics of white blood cell deformation as it relates to receptor-ligand binding kinetics associated with the inflammatory response. He joined the Naval Research Laboratory (Washington, D.C.) in 2004 first as a National Research Council Post-Doctoral Associate and then as a civilian employee of the U.S. Navy. His research interests include non-display applications of liquid crystal, such as electrically-driven soft actuators and multifunctional organic nanoparticles, and more recently, the investigation of exciton energy transfer along nanoscale architectures.

Igor L. Medintz received a PhD in molecular and cellular biology from the City University of New York in 1998. He was a postdoctoral fellow under Prof. R. A. Mathies at the College of Chemistry, University of California, Berkeley, where he focused on developing FRET-based genetic assays for microfabricated devices. Since 2004, he has been a Research Biologist at the Center for Bio/Molecular Science and Engineering of the U.S. Naval Research Laboratory in Washington, DC. Current research activities involve DNA-based energy transfer assemblies and understanding enzyme activity at nanoparticle interfaces.

1. Introduction

One rapidly growing area in bionanotechnology is focused on creating *de novo* light harvesting and energy transfer devices. The overarching theme here is to be able to carefully position multiple, and in many cases different, fluorophores on some type of well-defined bioscaffolding in an architecture that allows them to interact energetically with high transfer efficiency. Both the scaffold and energy transfer can then be characterized, optimized if needed and exploited to form the basis for different types of artificial light harvesting along with powering biosensing, catalytic, charge conversion, photosynthetic, theranostic, optical coding, and logic devices, to name but a few potential applications [1–7]. The use of defined structures to orient chromophores for optimized energy transfer is not new and indeed a rich library of utilizing dendrimers for such applications can be found [8,9]. In comparison to the synthetically intense approach of using dendrimers or analogous polymeric materials for attaching dyes into discrete controlled architectures, the use of biomolecular substrates offers several potential benefits that make them attractive for such applications. For example, biomolecular scaffolds such as viruses are highly symmetrical while DNA can be self-assembled into almost any arbitrary 3-dimensional structure. Moreover, in many cases, these scaffolds can be recombinantly or site-specifically modified with dyes to yield a particularly desired arrangement.

Cumulatively, the convergence of several factors has provided the necessary toolset for research toward these goals. First, the biotechnology revolution has provided facile access to designer proteins, peptides, DNA and the like. Second, wide access to the still growing suite of fluorophores including fluorescent proteins, large families of organic dyes (*e.g.*, rhodamines, Alexa Fluors and cyanines), semiconductor quantum dots (QDs), metal chelates, dye-doped and noble metal nanoparticles and fluorescent polymers. Third, the availability of many of these fluorophores in reactive or easily conjugatable form. Lastly, a growing number of site specific or chemoselective labeling chemistries for attaching such fluorophores to biomolecules in an intimately controlled, site-specific manner [10–14].

This review focuses specifically on nanoscale light harvesting and energy transfer devices built on biomolecular scaffolds and, thus, consists of two critical components. First, the scaffold within the nanoscale complex consists of biologically derived components. While the vast majority of structures and devices covered in this review utilize deoxyribonucleic acid (DNA), several other structures have been explored including cyclic peptides, virus capsids, and sugar complexes. In addition, a number of hybrid structures have been demonstrated, where inorganic components (most often QDs) are coupled to an organic component *via* biological scaffolding which can range from DNA to short peptide sequences. The second defining component is that the final assembled complex should demonstrate energy transfer either through multiple steps, *i.e.*, two or more, arising from at least three chromophores *and/or* which are patterned in an arrangement where several copies of two or more chromophores are engaged in energy transfer, see schematic in Fig. 1. The latter point is an important consideration given what is known about biological light harvesting systems. The most effective means of increasing energy transfer is to incorporate redundancy by increasing the probability of energy transfer through multiple pathways, each leading to a common terminal acceptor chromophore or chromophore complex [15].

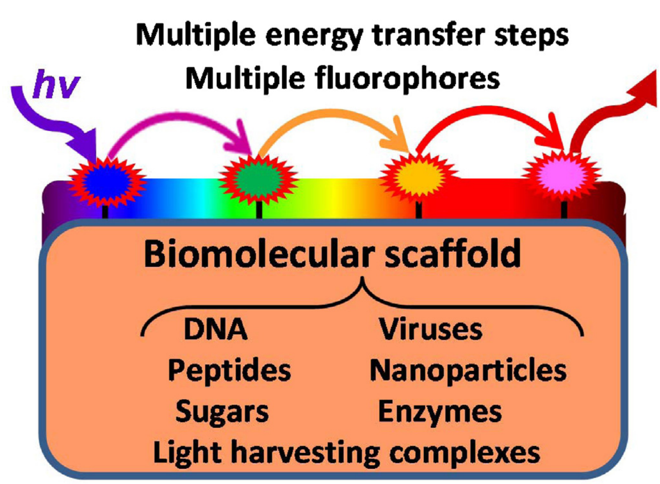

Fig. 1. Schematic summarizing various biological scaffolds and their role covered in this article. First, the scaffold or scaffolding material consists of biologically derived components. In addition, hybrid structures are included where inorganic components are coupled to an organic component *via* biological scaffolding which can range from DNA to short peptide sequences. For consideration here, the final assembled complex should demonstrate energy transfer either through multiple steps or is patterned in an arrangement where several copies of two or more chromophores are engaged in energy transfer.