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Bolaamphiphilic molecules: Assembly and applications

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ABSTRACT

This review describes the state-of-the-art scientific developments of bolaamphiphilic molecules composed of two hydrophilic headgroups connected by a hydrophobic chain in the middle of the molecule. In contrast to previous review articles, this review focuses on the discussion of the bolaamphiphilic molecules from assembly to applications in various fields. The main principles of the assembly structures of bolaamphiphilic molecules are discussed, both at interfaces, including air/water and liquid/solid, and in solutions. Since different interactions exist among hydrophilic or polar head groups of the molecules, and the complexity of different hydrophobic, van der Waals, $\pi-\pi$ interactions, etc., between the chains, the assembly structures of the bolaamphiphilic molecules in the solution are more complicated and are therefore discussed in more detail. Finally, current applications for several important structures and assembly mechanisms of the molecules are introduced.

Contents

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1. Introduction

Bolaamphiphilic molecules contain two functional head groups. The two hydrophilic head groups connect via a hydrophobic molecule chain, as shown in Fig. 1 [1]. Since they exhibit unique hierarchically self-assembled structures both at interfaces, including air/water (Langmuir–Blodgett, LB, film) and liquid/solid, and in solutions, the synthesis and application of bolaamphiphilic molecules has been extensively studied. In the last two decades, various synthetic methods have been developed to produce functional bolaamphiphiles which mimick their natural counterparts. More attention has been given to studies of their hierarchally organized structures and applications in various fields, including drug delivery, gene delivery, electronics, medical imaging, etc. In the gene delivery application, one end of the bolaamphiphilic molecules functionalized with amine groups interacts with negatively charged nucleotides (in DNA and RNA) and assembles vesicle structures through amphiphilic properties. Other research has focused on the development of nanoelectronics. Due to their bio-compatibility and controllable morphologies, peptide-based bolaamphiphiles have drawn considerable attention in nanoelectronics for their potential as soft templates for production of nanobuilding blocks with different properties such as metallic, and seminconducting. By comparison, carbon nanotubes, also showing great potential in this area, have well-known separation issues that present barriers to their further applications, in both semiconducting and metallic applications.

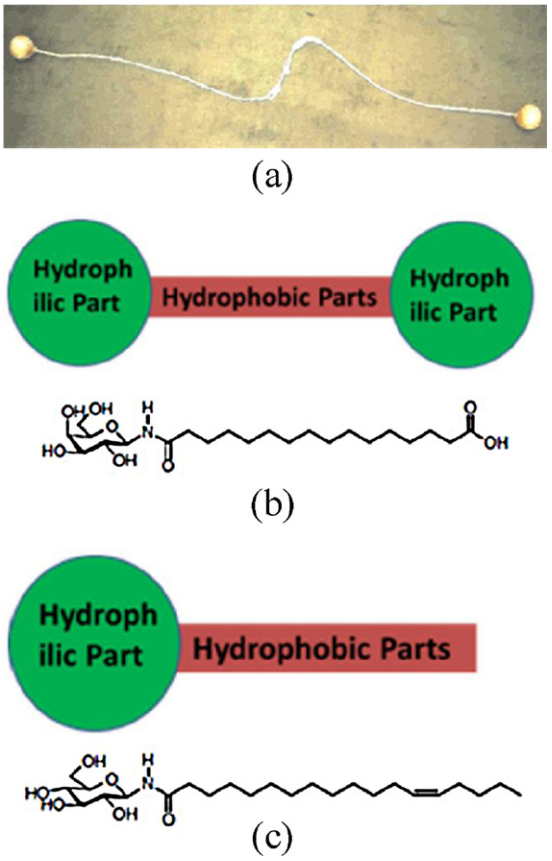

Fig. 1. (a) Photograph of an Argentinean bola with leather balls; (b) schematic drawing of defined bolaamphiphiles. Chemical structure below the diagram is an example of an unsymmetrical bolas; (c) a schematic drawing of an amphiphilic molecule which is not in the range of compounds of discussed here [1]. Copyright 2004. Reproduced with permission from ACS.

In this account, we define our subject, bolaamphiphilic molecules, as molecules that have hydrophobic repeating units connecting hydrophilic head groups at the two ends of the molecule, symmetrically or unsymmetrically. Therefore, our subject compounds include unsymmetrical bola-molecules as well. As shown in Fig. 1(b), a bolaamphiphile has two hydrophilic head groups: carboxylic acid and a glucose moiety. The hydrophobic connector consists of methylene repeating units which connect the two hydrophilic groups. As shown in Fig. 1(c), amphiphilic molecules, which have only one hydrophilic head group in the molecule, are not considered to be bolaamphiphilic molecules scope in this account. Bolaamphiphilic molecules in the definition of this account will be reviewed broadly focusing on their assembly structures and applications. Progress in the synthesis of such molecules is not a primary focus of this review. The review is divided into two main sections: Assembly (Section 2) and Applications (Section 3).

2. Assembly

Bolaamphiphilic molecules can self-assemble and form various hierarchal structures both at interfaces and in solutions since they possess both hydrophilic and hydrophobic portions. At interfaces, including air/liquid and liquid/solid, their assembly structures differ from those in a solution. Because of the special affinity of the hydrophilic groups in one phase, most important studies of bolaamphiphilic molecules at interfaces are particularly focused on monolayer formation at air/liquid or liquid/solid interfaces. For example, one-end-thiol-functionalized bolaamphiphilic molecules are widely studied on the formation of monolayer on gold substrate (Fig. 2). In addition, due to the molecules' amphiphilic properties, they can also