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Feature Article

Macromolecules based on recognition between cyclodextrin and guest molecules: Synthesis, properties and functions

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ABSTRACT

Highly stable inclusion complexes between cyclodextrin (CD) and guest molecules form due to their host–guest interaction. Polymer systems based on the complexes have been extensively reported in recent years. In this review, we highlight some recent advances from polymer systems with adamantane (Ada), azobenzene (Azo), ferrocene (Fc) and so on as guest molecules in terms of their synthesis, properties and functions. Various polymer topologies ranging from linear, branched, comb-like and hyper-branched are discussed in detail. In addition, the related systems with environmental stimuli-responsiveness and their potential applications are also presented.

Contents

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1. Introduction

In 1987, Pedersen [1], Cram [2] and Lehn [3] won the Nobel Prize in Chemistry due to their pioneering achievements in the field of supramolecular chemistry. Nowadays, supramolecular chemistry has attracted considerable attention as an important subdiscipline of chemistry from all over the world. On the basis of intermolecular noncovalent interactions including hydrogen bonds, hydrophilic and hydrophobic interaction, π–π interaction as well as electrostatic interaction, the research field of supramolecular chemistry is mainly about molecular recognition and the formation of ordered and functional structures by self-assembly [4]. The emergence of supramolecular chemistry provides a novel approach to create new substances, thus broaden the research scope of chemistry from a single molecule or several molecules to multiple-molecular systems. In 2005, a significant report [5] was published in Science on the subject of the 25 crucial scientific problems with which human beings have to confront in the 21st century, and self-assembly chemistry was included. It is crucial for supramolecular chemists to understand and control the assembly of reactant molecules in a bottomed-up manner, as what biological organisms do in nature.

Supramolecular chemistry originated from early coordination theory and the lock-key theory. In the late 1960s, the appearance of polyether and its recognition capacity to metal ions created the concept of host–guest chemistry [6,7]. Later on, many host molecules were developed, including crown ether, cyclodextrin (CD), calixarene, porphyrin, cyclic polypeptide, etc. Among them, CD [8,9], as the second generation of host molecules, has very excellent properties in terms of molecular recognition, molecular interaction and molecular aggregation. Many guest molecules with suitable sizes are able to have inclusion complexation with CD [10].

1.1. CD in supramolecular chemistry

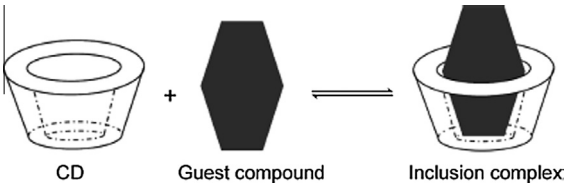
CD is a cyclo poly-saccharidemolecule with a large ring formed via end to end connection of α-1,4 glycosidic bonds of D-(+)-glucose unit. Due to the steric repulsion, CD generally has glucose units that is more than 6. General α-, β- and γ-CDs contain 6, 7 and 8 glucose units, respectively. The chemical structures of α-, β- and γ-CDs are shown in Scheme 1.

The three-dimensional structure of CD is like a truncated cone with all hydroxyl groups located at the surface of the molecule, making it soluble in water. On the other hand, the interior cavity of CD is relatively hydrophobic, allowing lipophilic molecules with proper size to be included by host–guest interaction (Scheme 2). Among the three common CDs, α-CD is apt to form stable supramolecular complex with monocylic aromatics, including azobenzene (Azo) and its derivatives; β-CD tends to interact with anthraquinone, cholesterol, ferrocene (Fc), adamantane (Ada), cyclic diene, Azo compound and some derivatives; γ-CD usually constructs supramolecular complex system with larger guest molecules, such as pyrene, anthracene, phenanthrene, steride and so on [10].

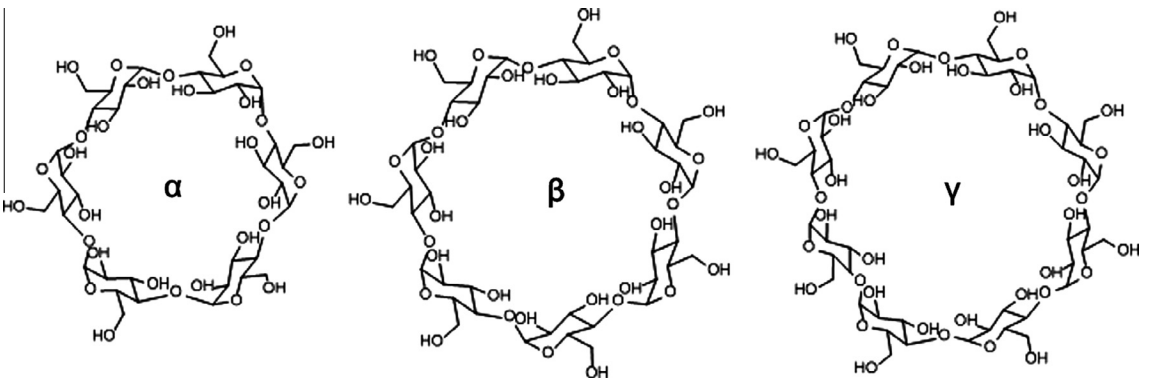
In fact, the host–guest interaction of CD derives from many aspects: hydrophobic interaction, Van der Waals interaction, ring tension of CD, surface tension of the solvent, as well as the effect of hydrogen bond [12–15]. This high availability, along with its low cost makes CD widely applied in various fields, including many disciplines such as pharmaceuticals [16–21], analysis [22,23], catalysis [24–26], and surface [27,28] as well as many industries like cosmetics [29], textile [30] and food [31,32]. Our group has been using CDs as a building block to construct some novel stimuli-responsive polymeric systems for many years [26,33–36].

1.2. Inclusion complexation of CD and Ada

Ada was isolated from petroleum in 1933. This alkane is a cage-like molecule with symmetrical structure and high



Scheme 2. Schematic representation of inclusion complex formation (1:1) between CD and a guest molecule. Reprinted with permission from [11]. Copyright (2009) American Chemical Society.



Scheme 1. Chemical structures of α-, β- and γ-CDs. Reprinted with permission from [11]. Copyright (2009) American Chemical Society.

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