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## TOWARDS THE SYNTHESIS OF CYCLODEXTRINS MODIFIED WITH SILICON (Si) AND TITANIUM (Ti) BASED COMPOUNDS FOR THE REMOVAL AND DEGRADATION OF ORGANIC CONTAMINANTS IN WATER

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### Abstract

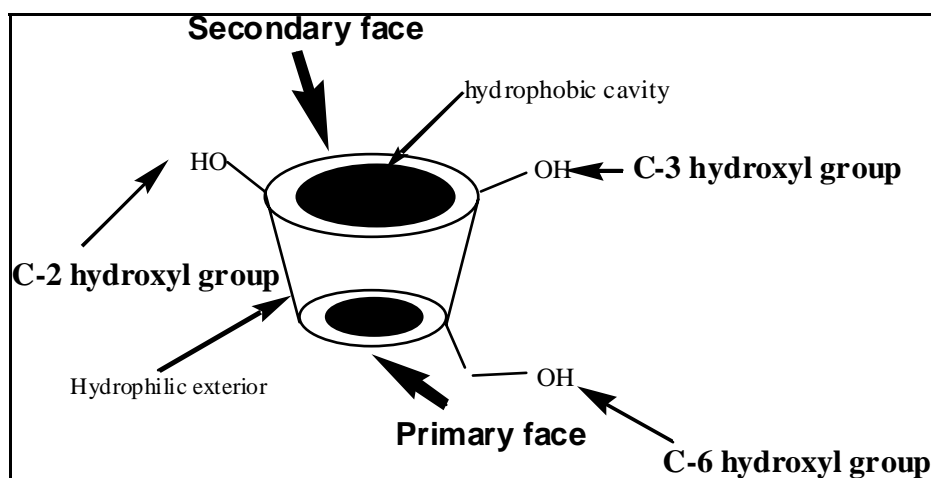
Cyclodextrins are a class of cyclic oligosaccharides. The most common types consist of six to eight glucose units linked through  $\alpha$ -1, 4-glycosidic linkages. They are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins (CDs), respectively. The use of cyclodextrin polymers has proved to be effective in the removal of organic contaminants from water. They form inclusion complexes with a wide variety of organic compounds. In this project, we synthesized cyclodextrin that possess Si and Ti pendent side chains. Polymerization of these CD derivatives with diisocyanate linkers is expected to produce Si- and Ti-based cyclodextrin polymers that are capable of absorption and degradation of the organic contaminants. It is envisaged that the silicon and titanium side chains will degrade organic contaminants while harboured inside the cyclodextrin cavity. The attachment of the Si and Ti pendent groups had been confirmed by the use of Fourier transform infrared (FT-IR) and Nucleic Magnetic Resonance (NMR) spectroscopic techniques. The reaction was monitored with thin layer chromatography (TLC).

**Keywords:** Cyclodextrin, hexamethylene diisocyanate, toluene 2,4-diisocyanate

## INTRODUCTION

### Cyclodextrins

The most common cyclodextrins (CDs) have six, seven and eight D-glucose units and are called  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CDs, respectively. They are usually referred to as first generation or parent CDs. These glucose units are interlinked by  $\alpha$ -1,4 glycosidic bonds thus forming a cyclic structure (1). A characteristic feature of the CDs is that they have a toroidal shape that forms well defined cylindrical cavities of about 8Å deep and 5-10Å wide. The cone is formed by the carbon skeleton of the glucose units and the glycosidic oxygen atoms that form the glucose units (2). The primary hydroxyl (OH) group of the glucose is located at the narrow end of the cone (primary face) and the secondary OH groups are located in the wider secondary face. The primary and secondary hydroxyl groups on the outside of the CD make them water-soluble. Cyclodextrins have an interior cavity that is hydrophobic and the exterior is hydrophilic. This feature allows for the encapsulation of various organic guests to produce host-guest complexes or supramolecular species in aqueous solutions (3). **Figure 1** shows the toroidal structure of a cyclodextrin.

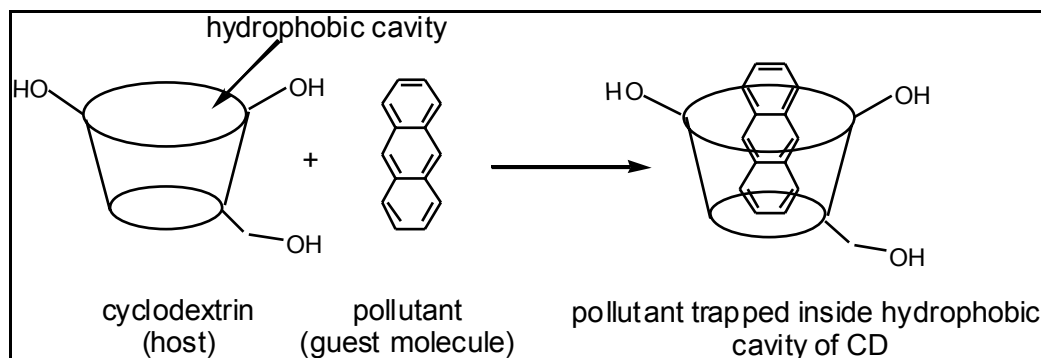


**Figure 1:** The toroidal structure of the cyclodextrin

### Formation of inclusion complexes

The interior cavity of the cyclodextrin provides a relatively hydrophobic environment into which an apolar pollutant can be trapped.  $\beta$ -CD based materials are known to exhibit high adsorption capacities toward phenolic molecules and dyes (4). They also form a wide variety of inclusion complexes with low-molecular-weight compounds, which range from apolar

and aliphatic hydrocarbons to polar carboxylic acids, and amines (5). The CD moiety can harbour various small, suitably shaped organic compounds in its tubular cavity by shielding the bound species from the surrounding aqueous environment (6). This phenomenon is a result of the hydrophobic interaction between the host cyclodextrin and the guest organic species and is illustrated in **Scheme 1** below.

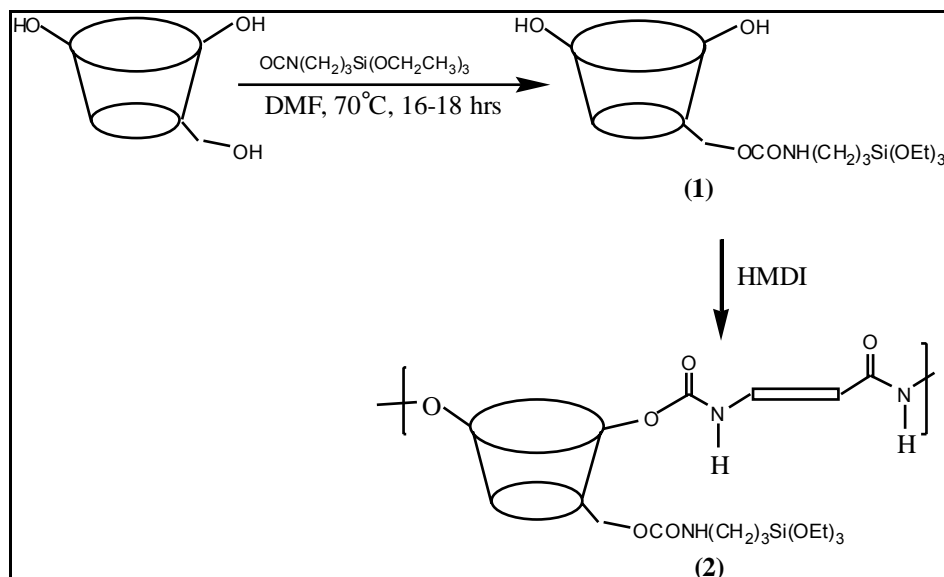


**Scheme 1:** The formation of the inclusion complexes

### Cyclodextrin Derivatives

The presence of hydroxyl (OH) groups on the outer cavity can be exploited in order to alter the physical and chemical properties of cyclodextrins. For instance, the functionalization of CDs can decrease their solubility in water, increase their stability in the presence of light, heat and oxidizing agents and also make them more volatile (6). The primary hydroxyl groups (OH-6) are more reactive than their secondary counterparts (OH-2 and OH-3). These hydroxyl groups are shown in **Figure 1**. The OH-2 hydroxyl groups are acidic and therefore more reactive than OH-3. Also, the OH-3 hydroxyl groups are not easily accessible thereby making them even less reactive. On the other hand, the primary hydroxyl groups attached to C-6 are basic and easily accessible. As a result, OH-6 hydroxyl groups are often more reactive during nucleophilic substitution reactions (6).

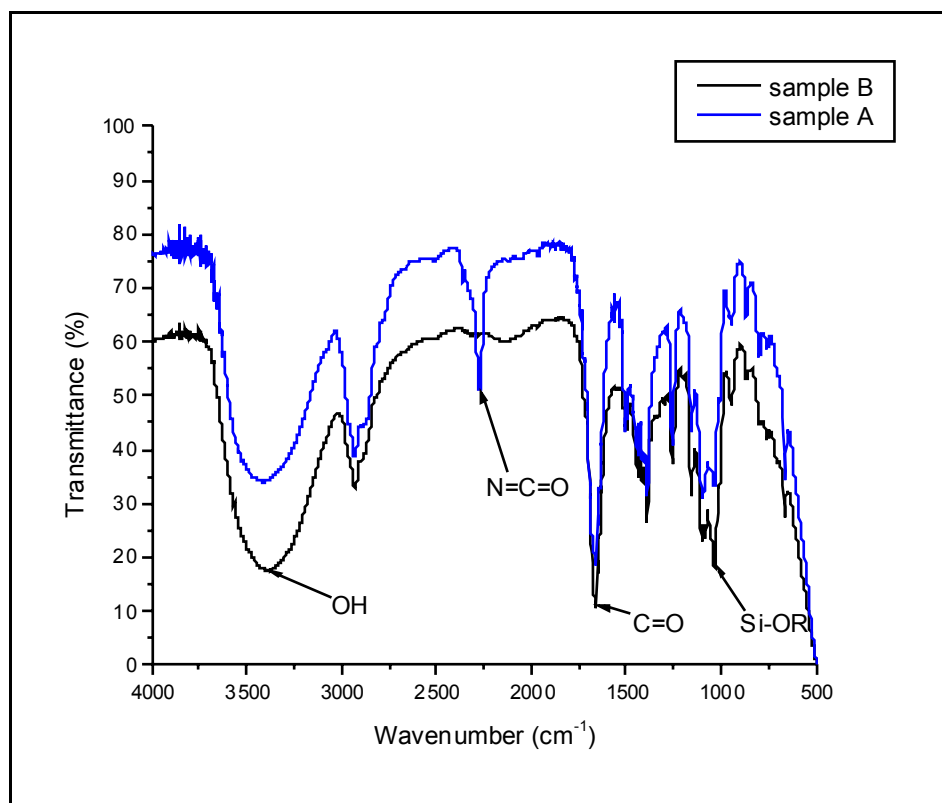
Herein we report on the synthesis of  $\beta$ -cyclodextrin-3-triethoxy-propyl silane **1**, a precursor for Si- and Ti-based  $\beta$ -cyclodextrin polymers. The synthetic route for this precursor is illustrated in **Scheme 2**. Reaction of this precursor with diisocyanate linkers is expected to produce the corresponding silylated  $\beta$ -cyclodextrin polymer **2**. The silicon unit of the polymer is expected to participate in the degradation of the organic pollutant.



**Scheme 2:** The synthesis of  $\beta$ -cyclodextrin-3-triethoxy-propyl silane precursor **1** and the corresponding Si-based polymer **2**.

Alternatively, nanoparticles of titanium dioxide ( $\text{TiO}_2$ ) can be attached to the silylated  $\beta$ -cyclodextrin precursor to produce a compound of the type **3**. The  $\text{TiO}_2$  nanoparticles have previously demonstrated catalytic, photocatalytic, and electrical properties (7). Therefore, it is envisaged that the  $\text{TiO}_2$  will enhance the degradation of organic pollutants under visible light. The two Si- and Ti-based systems (**2** and **4** in **Schemes 2** and **3**, respectively) will, therefore, perform the dual role of encapsulating the organic contaminants and degrading them whilst harboured inside the cavity of the cyclodextrin polymer.

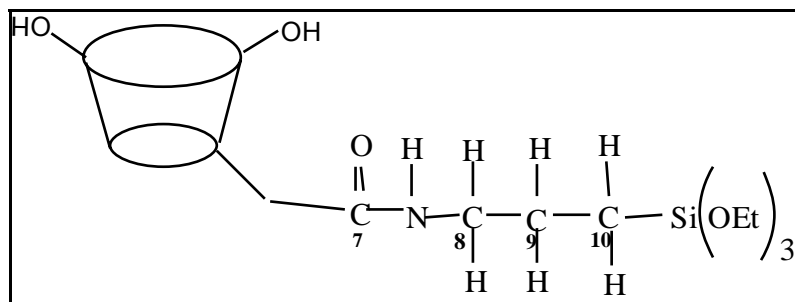




**Figure 2:** FT-IR Spectroscopy of  $\beta$ -CD-3-triethoxy-propyl silane

### Nuclear Magnetic Resonance

$^1\text{H}$  NMR spectroscopy provided more evidence for the formation of  $\beta$ -CD-3-triethoxy-propyl silane. New peaks that correspond to N-H, N-CH<sub>2</sub> and Si-CH<sub>2</sub> were observed (9, 10, 11). Compared to the Si-CH<sub>2</sub> triplet, which appears at -0.02 ppm, the N-CH<sub>2</sub> protons appear as a multiplet at 2.72 ppm. The electronegative nitrogen atom is obviously responsible for the deshielding of the N-CH<sub>2</sub> protons (9). The N-H triplet and the N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si multiplet were observed at 2.88 ppm and 2.08 ppm, respectively.



**Figure 3:**  $\beta$ -Cyclodextrin-triethoxy-propyl silane

### CONCLUSION

$\beta$ -Cyclodextrin-triethoxy-propyl silane, a precursor for Si- and Ti-based polymers, has been successfully synthesized. The disappearance of the isocyanate at  $2274\text{ cm}^{-1}$  provided evidence for the incorporation of the silyl unit onto the cyclodextrin. Other techniques such as IR, NMR, TLC and melting point provided more evidence for the formation of the silylated precursor. Polymerization of this precursor will provide access to polymers that possess the ability to absorb and degrade common organic pollutants.

### ACKNOWLEDGEMENTS

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