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Molecularly imprinted β-cyclodextrin polymer as potential optical receptor for the detection of organic compound

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ABSTRACT

A molecularly imprinted β-cyclodextrin polymer (MIβ-CDP) was synthesised using β-cyclodextrin (β-CD) as monomer that is cross-linked using toluene 2,4-diisocyanate (TDI); *N*-phenyl-1-naphthylamine (NPN) was used as the template molecule. The MIβ-CDP was fluorometrically characterised using a fibre optic cable attached to a self-designed flow-cell. The fluorescence emission spectrum of the MIβ-CDP was found to be associated with the activity of binding to NPN through batch rebinding analysis. Heterogeneous binding models (bi-Langmuir and Freundlich isotherms) that yield information on binding sites affinity distribution and heterogeneity index were employed to characterise this process. Analytical studies demonstrated that the fluorescence intensity was linear in the analyte concentration range up to 1.6×10^{-4} M with a limit of detection (LOD) of 1.38 μM. The non-linear response range was successfully modelled using a power relation that is similar to the Freundlich isotherm and the dynamic response was successfully extended to 2.0×10^{-3} M. The response time of the system was determined to be 90 s with an optimum flow of 0.02 mL s^{-1} and methanol as analyte solvent. Molecular imprinting efficiently promoted a better sensing signal by increasing the binding-affinity and substrate-selectivity towards the template molecule, compared with the control polymer prepared in its absence. The sensitivity was enhanced by about 16% as measured with three different concentrations of analyte. The sensing receptor was successfully regenerated using acetonitrile and can be reused with no significant decay in intensity with a relative standard deviation (RSD) value of 2.24% ($n = 13$). The sensor developed was successfully tested for analytical determination of NPN.

1. Introduction

In recent years, molecular imprinting has become an important technique in preparing of artificial and robust recognition materials [1–3]. Molecularly imprinted polymers (MIPs) are readily obtained by polymerising different functional monomers and cross-linkers in the presence of the template molecule. When the template molecule is removed, a highly specific micro-cavity will be formed within the rigid three-dimensional polymer matrix, which has high binding affinity toward the template molecule [2–5]. These polymers not only exhibit a tremendous thermal, chemical, and mechanical stability but also are able to mimic the property of natural systems such as enzymes or antibodies [6]. Due to these factors, molecular imprinting technology has gained much interest in different applications such as in analytical [7,8], catalytic [9,10], pharmaceutical [11,12] and separation [13,14] processes. As for optical sensors, the hybrid of this technology has given the merit of enhanced selectivity in sensing in a multi-analyte environment besides maintaining all the well known advantages of optical sensors [15,16]. It is worthy to note that prior to use of MIPs in real practical sensing application, the understanding and knowledge of these materials need to be obtained in order to maximise their performance in the sensing regime. This is because the properties of MIPs in practice often deviate from the theoretical concept of molecular imprinting technology, which introduce certain degree of complexity when used in real applications. For instance, MIPs typically contain binding sites that possess a wide range of affinities and selectivities although the imprinting concept may suggest a homogenous distribution of binding sites [17,18]. This binding site heterogeneity severely complicates the measurement of the binding properties of MIPs because it leads to binding that are highly dependent on the concentration range of the template analyte in which measurements are conducted. Besides heterogeneous sites, the bleeding of un-removed template during the application stage also found to be highly problematic. Therefore, all these deviating factors need to be considered and correlated within the same sensing system during the fabrication or at the application stage

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of the MIPs in order to produce a reliable and robust optical sensor.

Particularly in designing a MIP sensor receptor for organic compounds, β-cyclodextrin (β-CD) is an attractive candidate monomer for use as the building units for the matrix. Basically, β-CDs are cyclic oligosaccharides formed by the connection of seven individual D-(+)-glucopyranose units through α-1,4-glycosidic oxygen bridges (Fig. 1). The physical conformation of the molecular structure creates a lipophilic inner cavity with hydrophilic outer surfaces that is capable of interacting with a large variety of guest molecules to form non-covalent inclusion complexes [19–22]. Commonly, the formation of inclusion complex can alter the photo-chemical and photo-physical properties of the guest molecules that can be used as quantifiable signal [23]. In analytical application, β-CDs have been used extensively in conjunction with luminescence techniques because many analytes show enhanced luminescence quantum yields associated with the formation of complexes. In terms of MIP application, the hydroxyl group on the β-CDs structure can act as polymerisation terminal with a suitable cross-linker to form a stable polymer matrix. The arrangement of the β-CD moieties will be highly uniform as a result of the interactions with the template molecule that is added during the polymerisation process. This has been demonstrated by Komiyama and co-workers in their work using β-CD as monomer to imprint various steroid compounds [24–26]. Their main focus is to utilise the molecularly imprinted β-cyclodextrin polymer (MIβ-CDP) for separation of organic compounds. However, the potential of the MIβ-CDP in sensing application has not been highlighted or discussed, especially via optical detection approach.

In the work presented here, the potential of utilising β-CD as functional monomer to fabricate a MIP as sensing receptor has been investigated. The main motivation is to explore the synthesis of the MIβ-CDP from the viewpoint of its analytical capability, besides revealing the advantages and limitations of optical sensors having a receptor of this kind. Well-established batch binding analysis is employed to evaluate the binding properties of the imprinted polymer via bi-Langmuir and Freundlich binding models to yield a measure of binding sites affinity distributions and the heterogeneity index of the polymer. The binding properties obtained are correlated with the signal of the sensor to generate an understanding towards the analytical characteristic portrayed by the MIβ-CDP. In order to demonstrate this study, *N*-phenyl-1-naphthylamine (NPN) (Fig. 2) was chosen as the template molecule based on the following criteria. First, NPN molecule is fluorescent and therefore the signal can be used to monitor the binding event that occurs subsequent to template removal. Second, there have been some previous literature reports on the development of the analytical methods for the detection of NPN, which will be useful

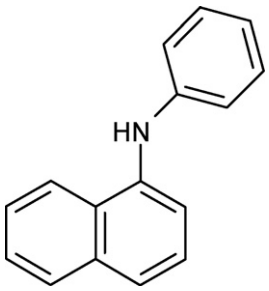

Fig. 2. Chemical structure of NPN.

in this study for comparison purposes [27–29]. Finally, due to the wide use of NPN in various materials (e.g., as antioxidant in rubber, grease, lubricating oil, transformer oil, and as raw material for the production of dyes and other organic chemicals), its release to the environment can cause pollution and therefore it will be an advantage if this study can contribute towards the development of a sensor that can be used to monitor NPN. This need became more pronounced as NPN is also believed to be carcinogenic and its effect towards health is of much concern [30–35].

2. Experimental and methodology

2.1. Reagents and chemicals

All chemicals and reagents used are of analytical grade unless otherwise stated. β-Cyclodextrin (β-CD) (Acros Organic) was dried at 110 °C under reduced pressure for 8 h before use. Anhydrous grade of *N*,*N*-dimethylformamide (DMF), anhydrous grade of acetonitrile (all from Sigma–Aldrich), toluene-2,4-diisocyanate (TDI) (Fluka), and *N*-phenyl-1-naphthylamine (NPN), (Acros Organic) were used as purchased. Double distilled deionised water was used throughout the study.

2.2. Apparatus and instrumentations

Shimadzu UV-2400-PC spectrophotometer was used for absorbance measurement that is digitised at 1.0 nm intervals. A cell of 1.0 cm absorption path length was used in these measurements with methanol as the optical blank solution. All fluorescence measurements were recorded using PerkinElmer LS55 spectrofluorometer with fibre optic accessory attached to the working flow-cell. Sample was injected into the cell using a standard low pressure micro-valve sample injector with the sample loop capacity of 0.5 mL. pH for solution was monitored using HI 9815 pH meter

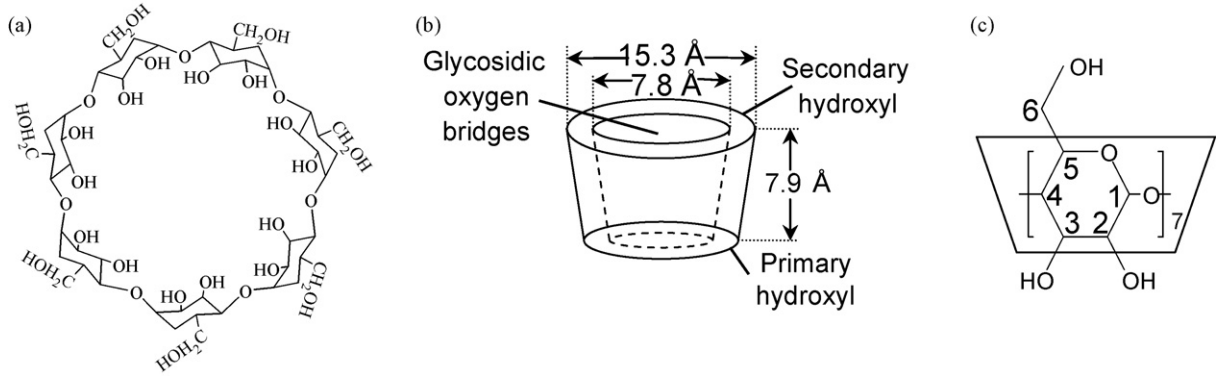

Fig. 1. The β-CD (a) chemical structure, (b) dimension and (c) carbon number assigned for each D-glucopyranose sub-unit.