FABRICATION OF ENANTIOSELECTIVE CHIRAL SENSOR USING MOLECULAR IMPRINTING APPROACH

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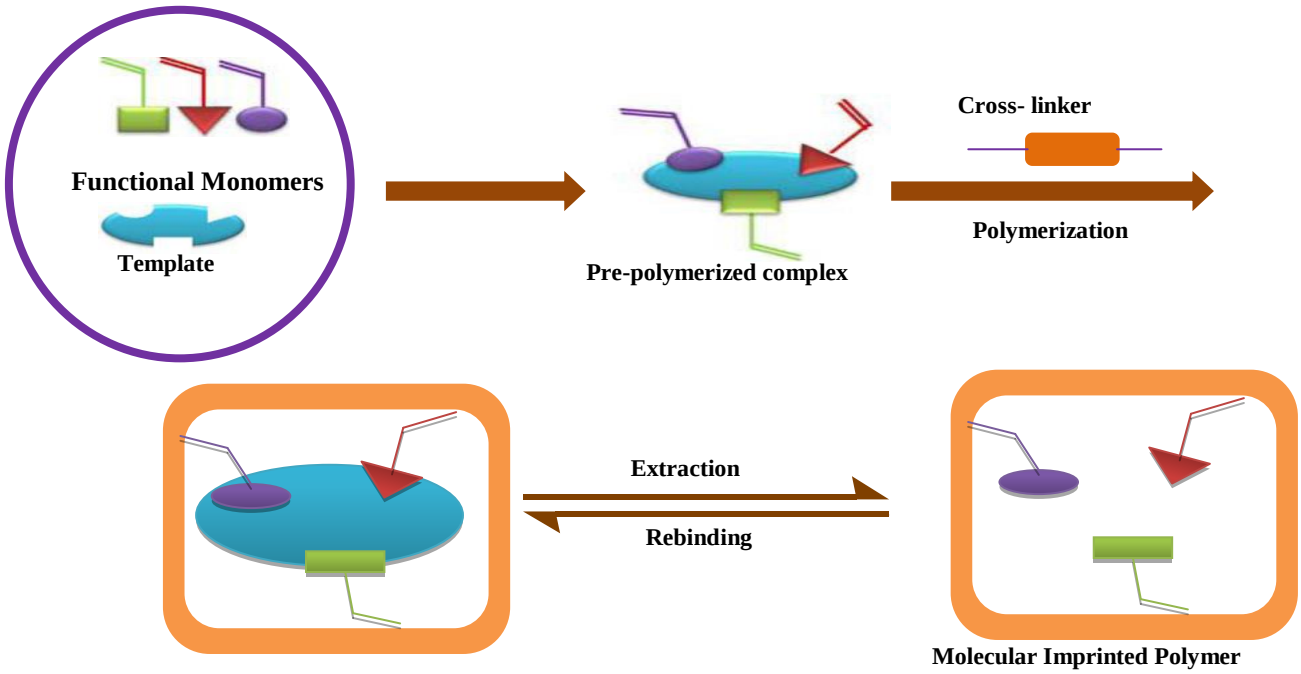
BRIEF SUMMARY OF THE PROJECT WORK

Chirality is an important universal phenomenon in nature. For the in-depth study of pharmacology and biology, efficient enantioselective technologies are essential. Research on enantiomeric recognition of chiral compounds can provide us important information to understand the recognition process in biological systems. Although some progress in chiral discrimination has been achieved during the past decades, the selective detection of individual enantiomer is still the most difficult analytical task owing to the similar physical and chemical properties and the similar molecular configurations of enantiomer. Hence it is important to fabricate practical and rapid available methods for the chiral recognition and separation of enantiomers.

α-Hydroxy carboxylic acids, which are the structural units of many natural products and drug molecules, represent one of the most important classes of chiral compounds in nature. As one of the α-hydroxy carboxylic acids, mandelic acid (MA) is a significant chiral analogue of amino acids in the pharmaceutical synthetic industry. Due to its bacteriostatic properties, it is employed for the treatment of urinary tract infections, i.e., from either the calcium or ammonium salt. It is present in certain skin care products and used as a precursor in the manufacture of certain dyes. The pure form of D-Mandelic acid (D-MA) is applied as a precursor for the synthesis of cephalosporin and penicillin. It is also used as a chiral resolving agent and chiral synthon for the synthesis of anti-tumour and anti-obesity agents. Mandelic acid and its derivatives are multifunctional precursors for synthesis of many optically pure amino acids, so an effective method for control of optical purity of this class of compounds is highly desirable. Although many approaches have been used for recognizing MA, designing a simple and efficient system for enantioselective recognizing MA enantiomer is still a challenging task.

Molecular imprinting is a promising technique for the preparation of polymers with predetermined selectivity, specificity and high affinity which involves arrangement of polymerizable functional monomers around a print molecule. Molecularly imprinted polymers (MIPs) have the ability to specifically distinguish and separate a particular molecule from other molecules of similar structures. This property makes MIPs applicable in various fields such as in separation and purification of structurally related compounds, catalysis, biosensors, drug delivery, and in biotechnology. A schematic representation of the molecular imprinting process is shown in Scheme 1.1.



Scheme1.1. Schematic representation of molecular imprinting.

The role of MIPs in chiral separation of racemic mixtures is most important because the classic techniques are not efficient for this purpose. Among the various approaches used during synthesis of MIPs non-covalent interaction can be considered the best one due to easy removal of template, applicable for a variety of molecules, economical and easy method. The main issues in molecular imprinting technology are its low selectivity, low response kinetic and large template size limitations. So many efforts were done to resolve these problems. One of the techniques is based on the small dimension with extremely high surface-to-volume ratio of nano-imprinting materials, which enable the imprinting technique to create more effective recognition sites than those obtained by traditional approaches which only use porogens. The imprinting of molecular recognition sites at nanostructures has greatly

improved the removal of templates and the binding capacities and kinetics of molecular recognition, compared with the traditional imprinted bulky materials.

Over the past decade, we have demonstrated the advantagesof ultra-thin films of TiO_2 gel as useful matrices for molecular imprinting of different organic and inorganic species, by focusing on the development of highly selective sorbents and chemical sensors. However, the selectivity needs to be substantially improved in order to apply this technique for efficient enantiomeric separation.

Here in this minor research project, a novel sorbent for enantioselective recognition for D-MA is successfully fabricated on nano thin film of TiO_2 via molecular imprinting approach. The results of the high adsorption amount TiO_2-MIP particles for D-MA adsorption suggest that the nanolayer MIP preparation on the surface of the thin film could improve the porous site availability compared to bulk polymerization. FT-IR spectroscopy, SEM and XRD confirmed the homogeneous formation of TiO_2-MIP binding sites. The adsorption kinetics of D-MA on TiO_2-MIP was in agreement with the second-order rate equation. The high separation factor suggest that non-covalent molecular imprinting with TiO_2 as supporting material is a promising method for analyzing chiral compound with a simple structure.

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