

MIP thin films on quartz crystal microbalance

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Introduction

Molecularly imprinted polymers, MIPs (fig 1) are attracting great research interests for the development of biomimetic sensors, as they are advantageous over biological molecules in their high stability and low preparation cost.

There are generally two different approaches to combine MIPs with a transducer: 1) to immobilize a ready-made MIP on the transducer using physical entrapment or chemical coupling, 2) to in situ assemble a MIP layer directly on the transducer surface.

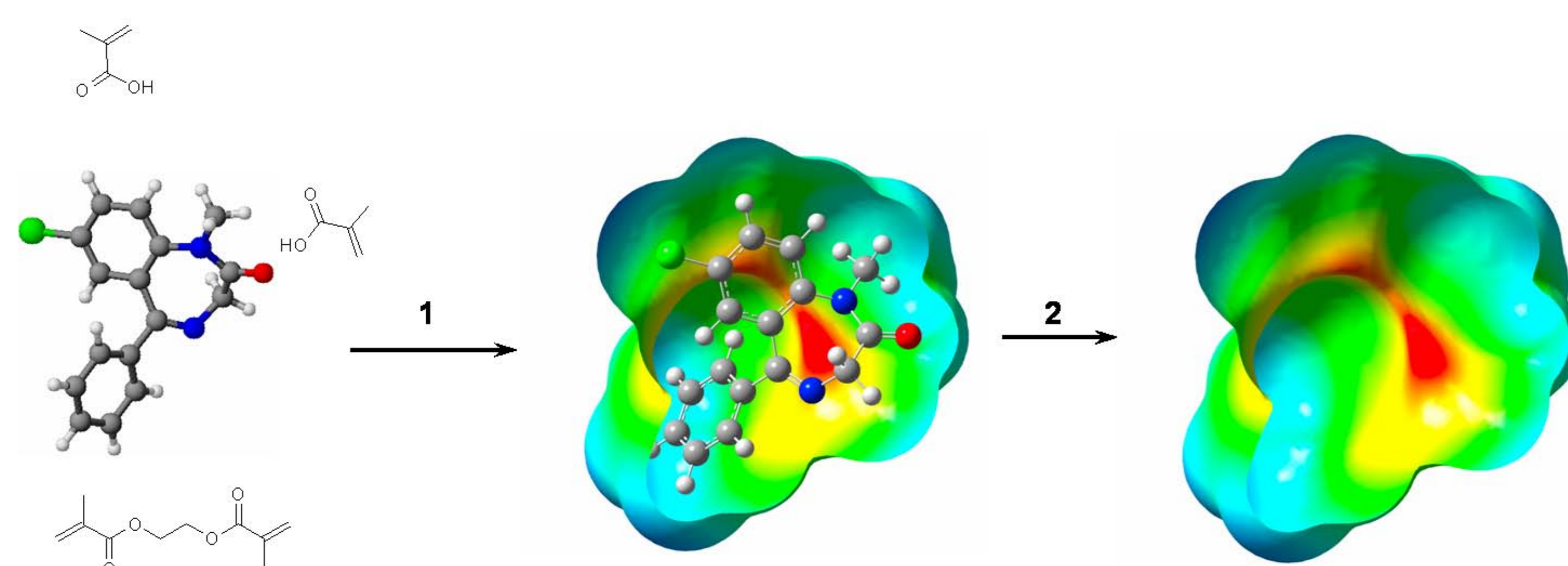


Fig 1. MIPs

The in situ assembly approach can be carried out on a small scale, and is often preferred when expensive chemicals (templates) are required. However, in most of the published procedures, the in situ MIP preparation has been difficult to control, giving large batch-to-batch variation.

In this study, we investigate a possible route to prepare ultra-thin MIP films using surface initiated radical polymerization.

Experimental Equipment

The Experiments use an Attana 100 continuous-flow biosensor and gold coated sensor chips.



Fig 2. Attana 100 system along with Attester software

Experimental Method

Polymer films are directly formed on the sensor chip (fig 3), offering effortless monitoring of polymer growth. Prior to polymerization, the photo-initiator is covalently coupled to a self-assembled monolayer of carboxyl terminated alkanethiol on a gold surface. A chiral drug, (S)-propranolol is used as template. Finally, test compounds are injected into the Attana 100 flow cell and the frequency shift is monitored.

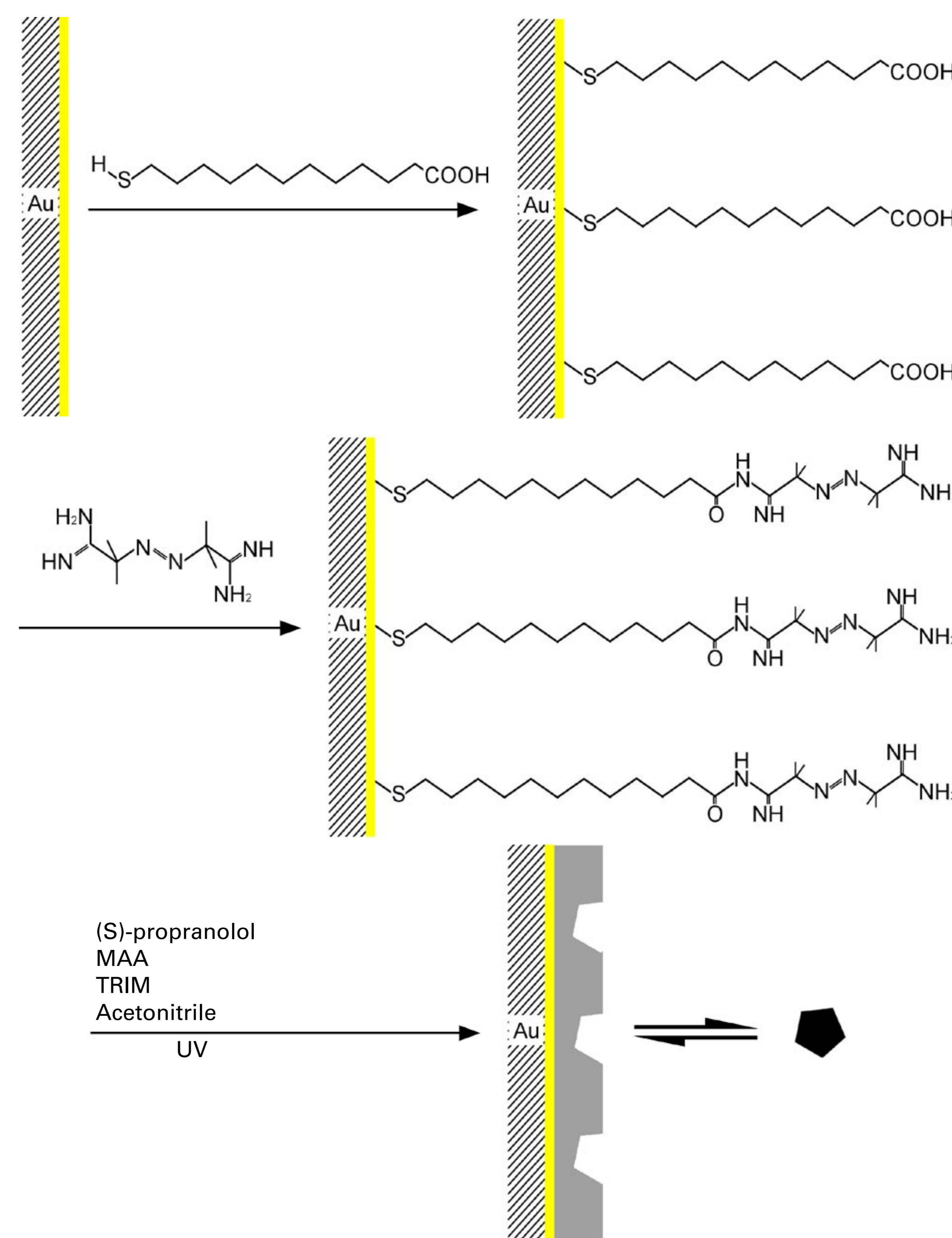


Fig 3. Preparation of molecularly imprinted polymer films using a surface bound photo-radical initiator.

Experimental Results

Crosslinked polyacrylate and polystyrene materials imprinted against (S)-propranolol have previously been shown to display chiral selectivity in aqueous solvents. In this study a film using 5% monomer in the imprinting reaction displayed chiral selective response at propranolol concentration of 0.38mM (Fig. 4). At the lowest concentration tested (0.19 mM), the QCM sensor generated a response of up to 50 Hz (Fig. 5). The binding is completely reversible, permitting repetitive injections of analytes without requiring surface regeneration.

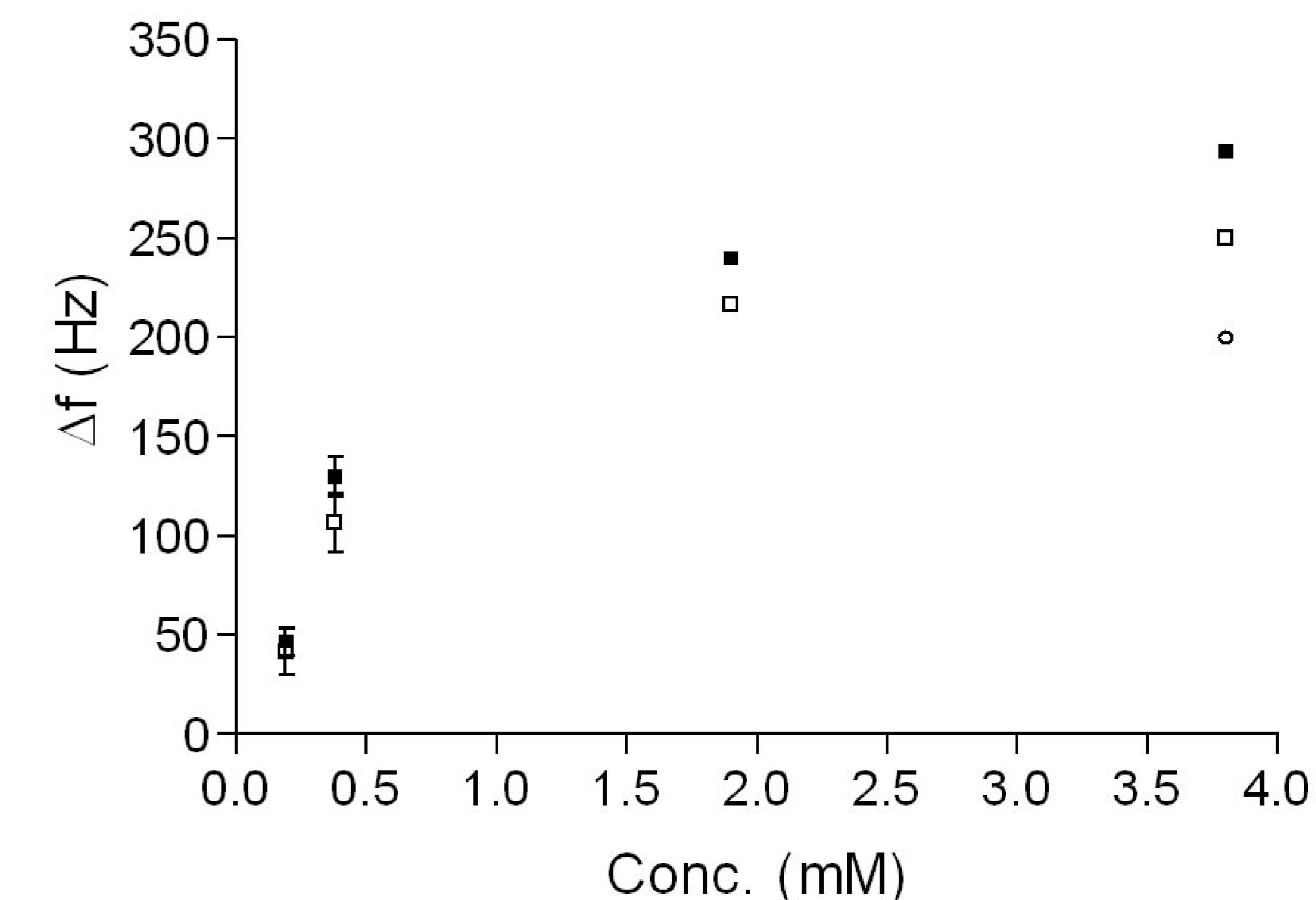


Fig 4. Frequency shift vs. concentration for target molecule, (S)-propranolol (solid square), and reference molecules, (R)-propranolol (open square) and artenolol (open circle), showing chiral selective response for (S)-propranolol.

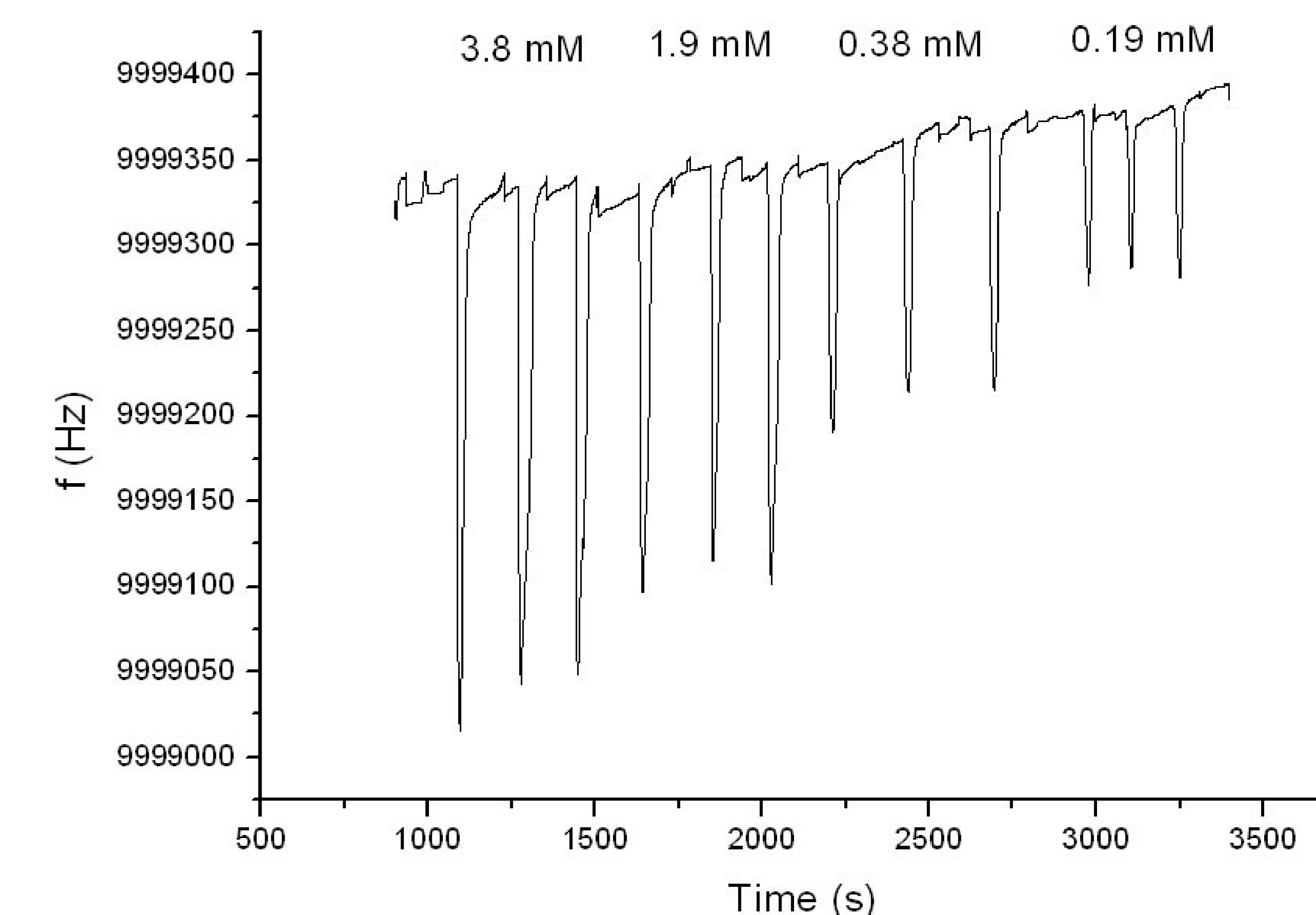
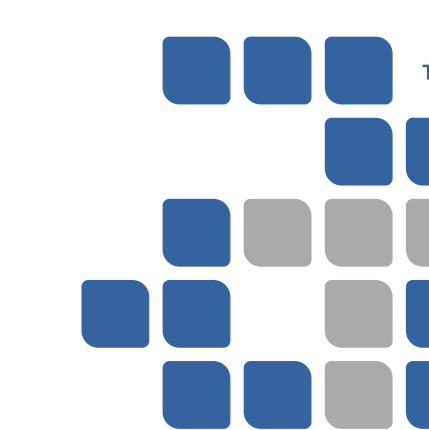


Fig 5. Real-time frequency response of (S)-propranolol injections on (S)-propranolol imprinted polymer surface showing rapid adsorption and desorption suitable for detection applications.

Conclusions

- In situ prepared MIPs on quartz crystal sensor with good reproducibility and long-term stability.
- Flexible MIP synthesis for effective control of polymer thickness.
- QCM sensor coated with MIP can be used for detection and discrimination between very similar molecules.
- Fast analysis and regeneration allowing large amount of samples.

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