

Abstract

# Self-Reporting Molecularly Imprinted Polymer for Label-Free Selective Electrochemical Sensing of *p*-synephrine †

Patrycja Lach <sup>1</sup>, Maciej Cieplak <sup>1,\*</sup>, Piyush Sindhu Sharma <sup>1</sup>, Marta Sosnowska <sup>1</sup>, Francis D'Souza <sup>2,\*</sup> and Włodzimierz Kutner <sup>1,3,\*</sup>

<sup>1</sup> Institute of Physical Chemistry, Polish Academy of Sciences (IPC PAS), Kasprzaka 44/52, 01-224 Warsaw, Poland; plach@ichf.edu.pl (P.L.); psharma@ichf.edu.pl (P.S.S.); m.i.sosnowska@gmail.com (M.S.)

<sup>2</sup> Department of Chemistry, University of North Texas, 1155 Union Circle, #305070, Denton, TX 76203-5017, USA

<sup>3</sup> Faculty of Mathematics and Natural Sciences, School of Sciences, Cardinal Stefan Wyszyński University in Warsaw, Wycickiego 1/3, 01-815 Warsaw, Poland

\* Correspondence: mcieplak@ichf.edu.pl (M.C.); francis.dsouza@unt.edu (F.D.); wkutner@ichf.edu.pl (W.K.)

† Presented at the 5th International Symposium on Sensor Science (I3S 2017), Barcelona, Spain, 27–29 September 2017.

Published: 4 December 2017

Molecularly imprinted polymers (MIPs) are excellent example of bio-mimicking recognition materials [1]. They have found numerous applications in selective chemosensing [2]. For electrochemical determination of electro inactive analytes, usually some external redox probe is added to the sample solutions. It is assumed that binding of target analyte molecules by MIP molecular cavities causes MIP film swelling or shrinking. This behavior leads to changes in MIP film permittivity for the redox probe and thus changes in faradaic currents corresponding to reduction or oxidation of the redox probe (so called “gating effect”) in CV and DPV determinations [3,4]. However, this mechanism seems to be inadequate for electrochemical sensors with conductive MIP film recognition units. For example, electrochemical impedance spectroscopy spectra recorded in our previous research [5,6] clearly indicate that redox probe diffusion to the electrode surface was not affected by analyte binding into MIP film. Moreover, well pronounced changes in charge transfer resistance were observed. These changes strongly suggest that drop of the redox probe oxidation peak in DPV determination originates from changes in electrochemical properties of the MIP film. Therefore, we can speculate that diffusion of a redox probe is a not crucial issue in terms of selective determination with the MIP film coated electrode. Therefore, a new specially designed monomer, viz., *p*-bis(2,2'-bithien-5-yl)methyl-ferrocene benzene was used for deposition of a self-reporting MIP film. This monomer acted as both a crosslinking monomer and an internal redox probe. It was electropolymerized together with 2,2'-bitiofen-5-carboxylic acid in the presence of the *p*-synephrine template—a diet supplement that is suspected of causing serious cardiovascular diseases. These self-reporting MIP film modified electrodes were used for electrochemical determination of *p*-synephrine in the absence of the external redox probe. For that, appropriate counterions were immobilized within the MIP either by lipophilic chromopropionic acid entrapment inside the MIP matrix, or by copolymerization of thiophene-2-methylsulfonic acid. In both cases, DPV measurements using PBS (pH = 7.4) showed oxidation of ferrocene at ~450 mV vs. Ag/AgCl and a relative change of the DPV peak current was proportional to the concentration of *p*-synephrine in the range of 10–100 nM with LOD equal to 5 nM.

## References

1. Cieplak, M.; Kutner, W. Artificial Biosensors: How Can Molecular Imprinting Mimic Biorecognition? *Trends Biotechnol.* **2016**, *34*, 922–941.
2. Uzun, L.; Turner, A.P.F. Molecularly-imprinted polymer sensors: realising their potential. *Biosens. Bioelectron.* **2016**, *76*, 131–144.
3. Yoshimi, Y.; Yoshiizumi, R.; Arai, R.; Nakano, I.; Sekine, S. Chiral-Discriminative Gate Effect in Self-Supporting Phenylalanine-Imprinted Poly(Methacrylic Acid-co-2-Vinylpyridine-co-Triethyleneglycol Dimethacrylate) Membrane. *J. Chem. Eng. Jpn.* **2009**, *42*, 600–606.
4. Yoshimi, Y.; Sato, K.; Ohshima, M.; Piletska, E. Application of the 'gate effect' of a molecularly imprinted polymer grafted on an electrode for the real-time sensing of heparin in blood. *Analyst* **2013**, *138*, 5121–5128.
5. Huynh, T.P.; Bikram, K.C.C.; Lisowski, W.; D'Souza, F.; Kutner, W. Molecularly imprinted polymer of bis(2,2'-bithienyl)methanes for selective determination of adrenaline. *Bioelectrochemistry* **2013**, *93*, 37–45.
6. Cieplak, M.; Szwabinska, K.; Sosnowska, M.; KC, C.B.; Borowicz, P.; Noworyta, K.; D'Souza, F.; Kutner, W. Selective electrochemical sensing of human serum albumin by semi-covalent molecular imprinting. *Biosens. Bioelectron.* **2015**, *74*, 960–966.



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).