ARC '16

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http://dx.doi.org/10.5339/qfarc.2016.HBPP2854

Carboxybetaine Ester Feature as a Platform for Switchable Surface Properties

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A lot of strategies for smart approaches on surfaces were applied such as hydrogel layer, polymer brushes or selfassembly monolayers (SAM) [1]. Nowadays switchable zwitterionic materials consisting of molecules with internally balanced charge between positive ammonium and negative carboxy group are promising candidates for this application [2]. They can combine antifouling properties of their zwitterion state and complexation or sticky character in their pre-zwitterionic carboxybetaine ester form. Zwitterionic forms possess antibiofouling properties due to electrostatic interaction between charged moieties, highly hydration capability and overall neutral charge in material as well as biomimetic character because zwitterions are structural similarity to biomembranes. We showed that modifications of surface by zwitterionic based self-assemble monolayer allow enhance detection limit of biosensors down to 10–15 M for analyte [3,4], or improve electrorheological response [5].

Carboxybetaine esters have cationic character and permit complexation with polyanionic bioabsorbents as well as character of counter ion can adjust wettability and interaction with biomolecules.

These studies will present on the utilization of pre-zwiterionic molecules: carboxybetaine based derivates formed from lipoic acid precursor in order to modify surface for construction of impedimetric lectin biosensors and for tuning wettability and interaction with DNA and other charged (bio)molecules.

Novel pre-zwitterionic carboxybetaine ester (hydrolysable and photolysable) derivates were synthetized by protocol consists of several synthetic steps and fully characterized. Subsequently, modification of a gold surface was performed by a self-assembled monolayer deposited from a solution containing prezwitterion molecules. Self-assembly monolayer, formed from derivates, was characterized by set instrumentation as atomic force microscopy, quartz crystal microbalance XPS, contact angle etc.

Hydrolysable carboxybetaine derivate was able to from complex with polycationic DNA molecules to preconcentrate and release at pH dependent manner. During course of hydrolysis carboxybetaine ester is transferred to

Cite this article as: Kasak P, Ilcikova M, Bertok T, Tkac J. (2016). Carboxybetaine Ester Feature as a Platform for Switchable Surface Properties. Qatar Foundation Annual Research Conference Proceedings 2016: HBPP2854 http://dx.doi.org/10.5339/qfarc.2016.HBPP2854.



Qatar Foundation لإطــلاق قــدرات الإنـــســان. Unlocking human potential

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carboxybetaine zwitterionic form to promote DNA release due to formation of carboxylate negative charge. Additionally, gradient in wettability can be observed within progress of hydrolysis and present of long perfluorinated or aliphatic types of counter ions. For example switch in wettability can be achieved only by simple and rapid couterion exchange between superhydrophilic (contact angle (CA) below 10° (to very high hydrophobilic (CA over 140°) on rough gold surface. After completed hydrolyses zwitterionic surface can be utilized as a platform for biosensor surface with nonfouling properties. Carboxylic functionality allows immobilizing sensing molecules as lectins for electrochemical impedance spectroscopy by means of EDC/NHS chemistry. This methodology provides opportunity for ultrasensitive detection up to 10–15 M of lectins which may result of a biomarker discovery on several diseases in whole media.

Moreover utilization of photolabile ester of carboxybetaine derivates allowing spatially control wettability and pattering with photomask was performed. Photolabile 2-nitrophenyl methyl ester group was introduced to pre-zwitterionic molecule and after irradiation of prepared surface with light at 365 nm was transformed from carboxybetaine ester group to zwitterionic carboxybetaine. Progress of photolysis can be observed by change of surface zeta potential, quartz crystal microbalance and contact angle measurement. This irreversible switch along with different interaction of biological species before and after photolysis will be discussed in this contribution as well.

This contribution was made possible by NPRP grant 6-381-1-078 from the Qatar National Research Fund (a member of the Qatar Foundation). The statements contained are entirely the responsibility of the authors.

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