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Quantum Dots-based competitive assay for the recognition of nucleotides

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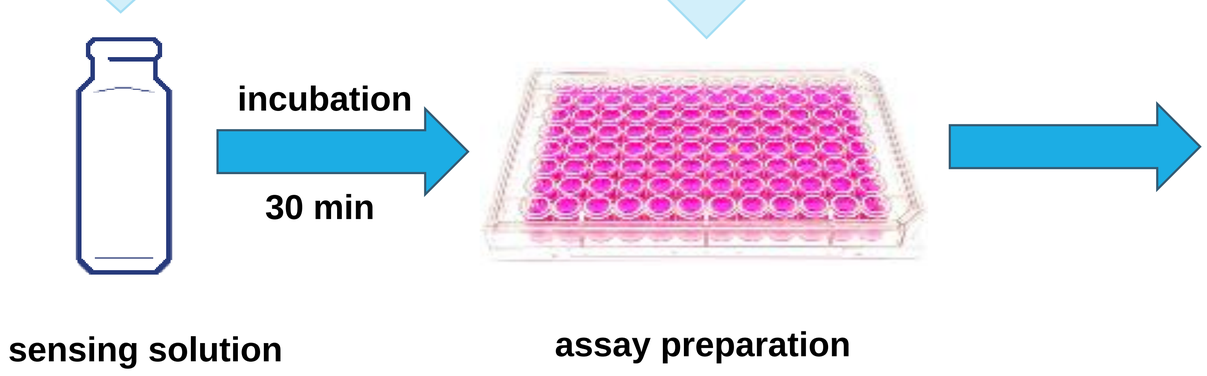
Introduction

Quantum dots (QDs) are colloidal, semiconductor nanocrystals with a diameter in the range of 1-20 nanometres, distinguished by unique physicochemical properties, which are partly the result of the extremely high surface-to-volume ratio and the quantum confinement effect. Due to their extraordinary optical properties, not only have they become an alternative to the commonly used molecular probes in biomedical applications, but they are also extensively studied nanomaterials for the development of sensing systems in analytical chemistry. Therefore, over the last few years quantum dots were employed in sensing systems representing many different detection schemes [1]. One of the promising sensing approach in which QDs can be implemented are Indicator Displacement Assays (IDA), where competitive interactions between sensing system elements are usually utilized.
In this work, a simple, quantum dots-based competitive assay for the recognition of nucleotides (AMP, ATP, CMP, CTP, UMP, UTP) is presented. The developed assay was constructed using single, thiomalic acid (TMA) capped CdTe quantum dots combined with nickel ions. The introduction of nucleotides into the sensing system resulted in subtle changes in fluorescent properties observed utilizing Excitation-Emission Matrix fluorescence spectroscopy. The obtained Excitation-Emission Matrixes (EEMs) were then used as characteristic, fluorescent fingerprints and processed by means of chemometric tools for nucleotides recognition. The presented results are a solid foundation for the development of a simple Indicator Displacement Assay (IDA) sensor array, which may serve as a tool for the identification and quantification of nucleotides in the future.

Experimental setup

- **HEPES** (10 mM, pH 7.4)
- **QD-TMA** (25 µg/mL)
- **Ni^{2+}**(80 µM)

AMP, ATP, CMP, CTP, UMP, UTP
(100 µM)



Fluorescent fingerprints

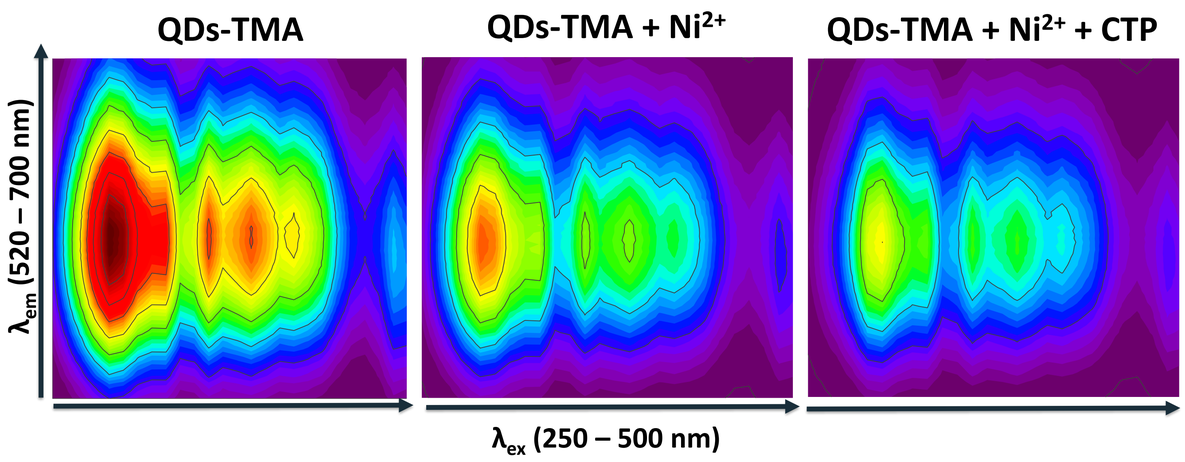


Fig 1. The change of QDs-TMA fluorescent fingerprints (EEMs) after the addition of the nickel ions (80 µM) and nucleotides (100 µM).

Recognition of nucleotides

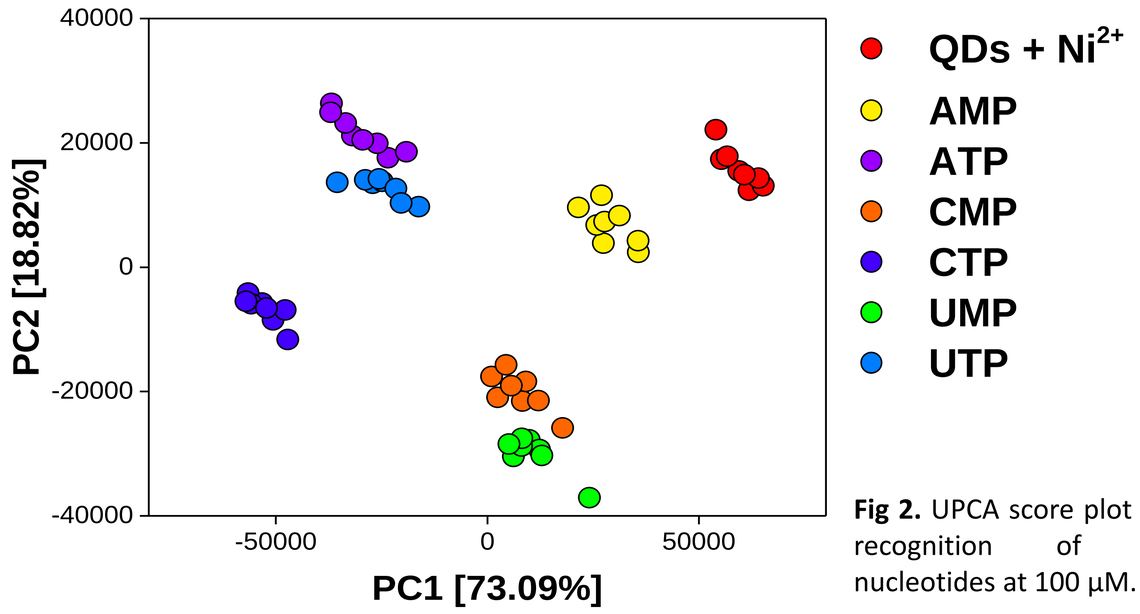


Fig 2. UPCA score plot for recognition of six nucleotides at 100 µM.

Conclusions and future work

- The developed detection system is based on the quenching of the fluorescence of QDs-TMA by nickel ions, and then observing further changes in the QDs-TMA + Ni^{2+} fluorescence response under the influence of nucleotides (AMP, ATP, CMP, CTP, UMP, UTP).
- The use of Excitation-Emission Matrix (EEM) fluorescence spectroscopy as a detection technique allowed to capture subtle differences in the way nucleotides interact with QDs-TMA + Ni^{2+} sensing element.
- Unfolded Principal Component Analysis (UPCA) showed that presented approach might be useful for the development of QDs-based competitive sensory array, which may serve as a tool for the identification and quantification of nucleotides in the future.
- Further works with other types of metal ions are ongoing in our laboratory in order to develop QDs-based sensor array for the detection of an extended pool of nucleotides.

Acknowledgements

This work was financially supported by National Science Centre (Poland) within the framework of the SONATA BIS project no. UMO-2018/30/E/ST4/00481 and the Warsaw University of Technology under the program Excellence Initiative, Research University (IDUB), BIOTECHMED-1 project no. 504/04496/1020/45.010401. Klaudia Głowacz acknowledges financial support from the IDUB project (Scholarship Plus programme).

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[1] Chern, M., Kays, J.C., Bhuckory, S., Dennis, A.M., Sensing with photoluminescent semiconductor quantum dots, Methods Appl. Fluoresc., 2019, 7, 012005.