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Chemically-Modified Cellulose Paper as Smart Sensor Device for Colorimetric and Optical Detection of Hydrogen Sulfate in Water

Jordi Rull-Barrull,^{a†} Martin d'Halluin,^{a†} Erwan Le Grogneq,^a François-Xavier Felpin^{a,b*}

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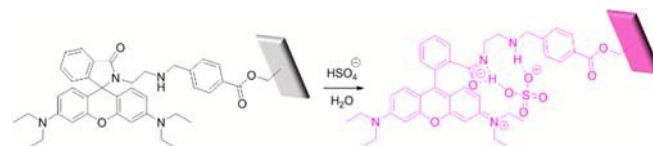
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A portable, recyclable and highly selective paper-based sensor device for the colorimetric and optical detection of hydrogen sulfate anions in water was developed. The detection system features a rhodamine-based sensor covalently grafted onto the highly hydrophilic surface of cellulose paper.

The selective sensing of inorganic anions and metallic cations is an area of growing interest, mainly because it has considerable applications for environmental and biological purposes.¹⁻⁷ In occupational settings, the detection of anions and cations is usually achieved with inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). While excellent limits of detection can be reached, these techniques suffer from the use of expensive instruments, hazardous sample preparation and require highly trained operators. Chemosensors allowing colorimetric and/or optical detection are particularly appealing technologies since they feature operational simplicity and low detection limits. Many anion-selective chemosensors have been designed and synthesized, especially for the recognition of fluoride and cyanide anions because their high nucleophilic properties are often exploited in the detection systems.^{5, 6, 8} By contrast, the sensing of hydrogen sulfate anions has been much less studied likely because its amphiphilic properties make the design of a selective chemosensor more complex. The detection of hydrogen sulfate anions is of primary importance in environmental science since they lead to unit outage in coal-fired power plant,⁹ affect adversely the vitrification process in radioactive waste remediation¹⁰ and are found in many fertilizers, contaminating cultivated grounds. Chromogenic sensors specific to HSO₄⁻ anions have been designed following two different strategies through metal-ligand coordinative interaction¹¹⁻¹³ and hydrogen bonding,¹⁴⁻²¹

leading to fluorescent enhancement (turn-on receptor) or fluorescence quenching (turn-off receptor). None of these chemosensors works in water, without any organic co-solvent, due to the large energy of hydration of HSO₄⁻ anions and the low solubility of the organic sensor. Since chemosensors-based technologies specific to hydrogen sulfate anions allow solution-phase sensing only and require the use of organic solvents, they are still far from real applications. Therefore, for real on-site sensing of hydrogen sulfate-containing aqueous samples, the design and the fabrication of solid supported sensors, offering both colorimetric and optical detection, high selectivity, portability and operational simplicity for use by low-skilled operators, are of great interest.

We reasoned that taking advantage of the amphiphilic properties of HSO₄⁻ anions for the design of a specific chemosensors covalently anchored onto a solid support would set up for a groundbreaking approach, unexplored so far. In this contribution, we disclose the design and the fabrication of a smart paper-based analytical device, enabling real on-site sensing of HSO₄⁻ anions in aqueous samples. The system features a rhodamine-based sensor, covalently anchored onto the highly hydrophilic surface of cellulose paper. Upon opening into its deep colored form in the presence of amphiphilic HSO₄⁻ anions, our specifically designed chemosensor exhibits both hydrogen bond receptor and donor sites as depicted in Scheme 1. We selected cellulose paper as platform for the sensor since it features low cost, water compatibility, portability, and disposability.



Scheme 1 Representation of the general strategy.

The surface functionalization of paper requires the chemical modification of hydroxyl groups from glucose units, but the dense hydrogen bond network and the bulk nature of paper strongly decrease their reactivity compared to soluble or highly dispersed polysaccharides. Therefore, prior to the surface functionalization, Whatman® #6 filter papers, exhibiting a high

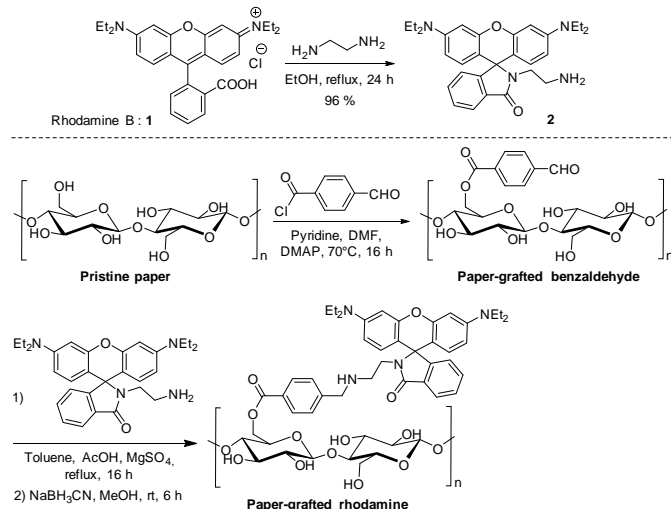
^a Université de Nantes, UFR Sciences et Techniques, UMR CNRS 6230, CEISAM, 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France. Fax: (+33) 251 125 40; E-mail: fx.felpin@univ-nantes.fr.

^b Institut Universitaire de France, 103, Boulevard Saint-Michel, 75005 Paris Cedex 05, France.

[†] These authors contributed equally to the project.

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content of α -cellulose and a medium density ($\sim 100 \text{ g/m}^2$), were soaked for 24 hours in 10% NaOH aqueous solution to break hydrogen bonds, increasing both the surface area of cellulose fibers and the reactivity of hydroxyl groups.²² The activated paper was functionalized with benzaldehyde groups by esterification of hydroxyl functions with 4-formylbenzoyl chloride (Scheme 2). We assume that the esterification mainly took place on primary alcohols, certainly more reactive than the remaining secondary alcohols of glucose units. The paper-grafted benzaldehyde was subsequently treated with rhodamine-ethylenediamine **2**, easily obtained by refluxing rhodamine B with ethylenediamine,²³ under reductive amination conditions, affording the expected analytical device. The degree of substitution was determined by elemental analysis to be ca. 4%, meaning that one hydroxyl group is functionalized with a rhodamine sensor every 25 glucose units. This value could be estimated to be somewhat low, but it ensures conserving both the physical integrity and the whiteness of paper.



Scheme 2 Preparation of the paper-based analytical device

The successive chemical modifications of the cellulose paper was followed and ascertained by FT-IR as depicted in Fig. 1. The spectrum of pristine paper exhibits characteristic absorption bands of cellulosic material in the region of 3400, 2900 and 1100 cm^{-1} accounting for the stretching vibrations of O-H, C-H and C-O-C bonds respectively. The grafting of the cellulose paper with benzaldehyde groups through an ester ligation was clearly evidenced by the apparition of new bands at 1723 and 1700 cm^{-1} in the region of carbonyls, attributed to the C=O stretching frequency of ester and aldehyde groups respectively. The band at 1204 cm^{-1} was assigned to the C-O stretching of the ester group. The grafting of rhodamine was confirmed by the apparition of three characteristic band of rhodamine at 1654, 1634 and 1613 cm^{-1} accounting for the stretching vibrations of the C=O bonds of the lactam group and aromatic C=C bonds. The integrity of the cellulose fibers was essentially not affected by the three successive chemical steps required for the preparation of the sensor device, as evidenced by the representative scanning electron microscopy (SEM) images presented in Fig. 2. The diameter of fibers in pristine and

grafted-papers are in the range of 8-14 μM (Fig. 2a-c). The direct consequences for preserving the structure of fibers are important since the grafted-paper is not wrinkled and the whiteness is preserved, allowing a high contrast for the colorimetric detection (vide infra).

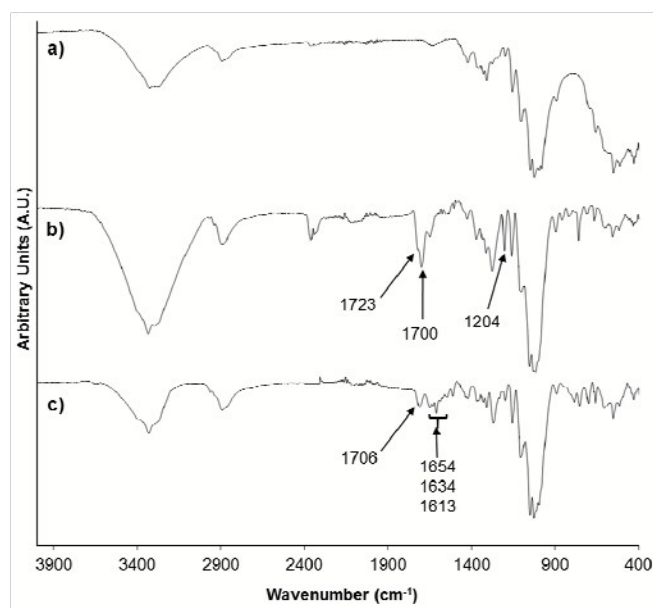


Fig. 1 FT-IR spectra of a) pristine cellulose paper, b) paper-grafted benzaldehyde and c) paper-grafted rhodamine.

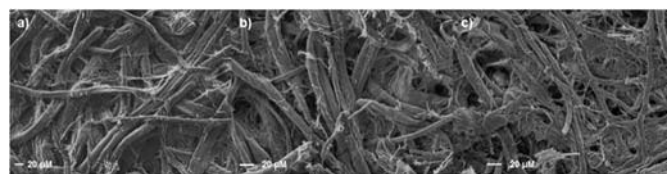


Fig. 2 SEM images of a) pristine paper, b) paper-grafted benzaldehyde and c) paper-grafted rhodamine.

Analysis of the surface composition of the material by X-ray photoelectron spectroscopy (XPS) after each chemical step, confirms the successful grafting of the rhodamine sensor. Full scan spectra of pristine paper and paper-grafted benzaldehyde only display carbon and oxygen element, suggesting that adsorbed salts, reactants and solvents were efficiently removed during the washing steps. The full scan spectrum of the paper-grafted rhodamine showed the presence N 1s peak, confirming the grafting of the sensor. High resolution spectra of C 1s region proved the successful surface modification with the significant increase of the peak accounting for C-C bonds at 283.9 eV and the apparition of a peak at 288.5 eV attributed to carbonyl functions (Fig. 3d,f vs. Fig. 3b).

With this new analytical device in hand, we investigated the colorimetric detection of anions. Colorimetric assay is the simplest technology in the quest of low-cost, portable and disposable analytical devices dedicated to on-site naked-eye detection. As expected, an intense pink color appeared on the paper strip dipped in a solution of hydrogen sulfate at 30 mM while the coloration response was not affected in the presence of other anions (HPO_4^{2-} ,

CN⁻, Cl⁻, F⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, AcO⁻ and OH⁻) in solution in water at 30 mM (Fig. 4a).

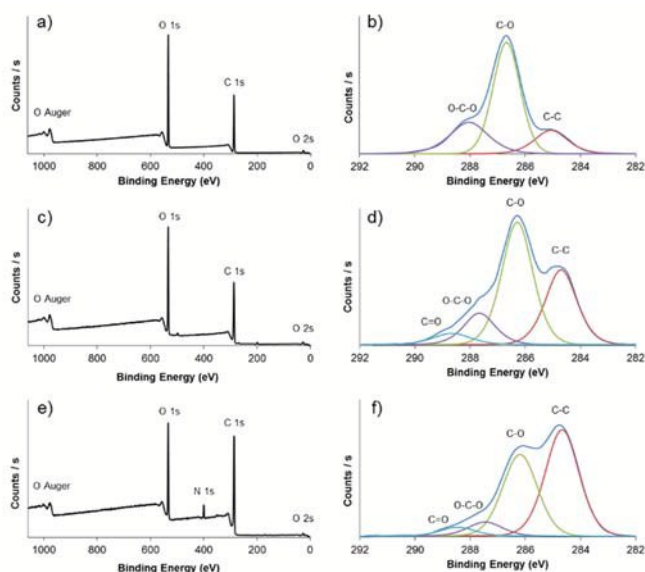


Fig. 3 Survey scan spectra of a) pristine paper, (c) paper-grafted benzaldehydes and e) paper-grafted rhodamine. High resolution C 1s spectra of b) pristine paper, d) paper-grafted benzaldehyde and f) paper-grafted rhodamine.

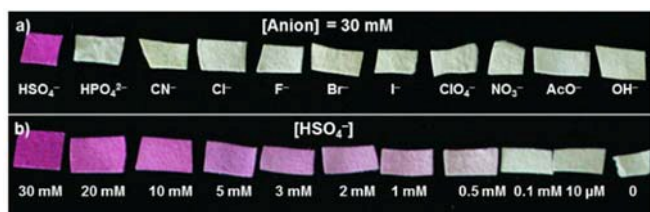


Fig. 4 a) Colorimetric detection of tetrabutylammonium salts in water at 30 mM through simple naked-eye analysis of the dipped paper strip. b) Effect of the concentration of HSO₄⁻ anions on the color change of the paper strip.

A color gradient from deep pink to pale rosy was clearly observed upon decreasing the concentration of HSO₄⁻, allowing a semi-quantitative estimation of the sample concentration in water by simple visual analysis (Fig. 4b). The limit of detection by naked eye is in the range of 0.1-0.5 mM. We stress, that the determination of the HSV or HSL color coordinates from the RGB color model could be used for quantification.^{24, 25} In a second time, we assessed the UV-vis spectroscopic properties of the paper strip. Upon immersion in distilled water, in the absence of anions, a very weak absorption band at ca. 560 nm was observed (Fig. 5a). By contrast, in the presence of 30 mM of hydrogen sulfate anions the sensor device showed a broad absorption band with a maximum at 564 nm, attributed to the open form of rhodamine as a monomer. Moreover, the shoulder at ca. 533 nm also suggests the presence of several aggregated forms on the cellulosic material.²⁶ Since the development of an analytical device, expected to be used in real conditions, requires a high selectivity, we further studied the cross-response of the paper strip to a large selection of anions such as OH⁻, NO₃⁻, I⁻, Br⁻, Cl⁻, F⁻, CN⁻, ClO₄⁻, HPO₄²⁻ and AcO⁻ in water at 30 mM. The sensor selectively recognized HSO₄⁻, since the absorptions of the paper strips, dipped into the solutions containing the anions, were essentially not affected compared to the paper immersed in the

anion-free water solution (Fig. 5a-b). Remarkably, even at a high concentration of anions (30 mM), the sensor device was not sensitive to HPO₄²⁻. The good recognition of sulfate vs. phosphate deserves emphasis, since the ability of both anions to interact with sensors through hydrogen bonding often led to poor discrimination.^{10, 11, 14, 27} The high discrimination of our device for HSO₄⁻ with respect to HPO₄²⁻ is attributed to the poor ability of HPO₄²⁻ to interact with the sensor due to its lower hydrogen donor properties.

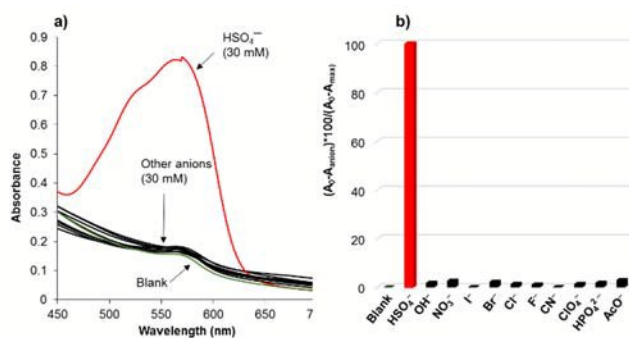


Fig. 5 a) UV-vis absorption spectra of the paper strip dipped into aqueous solutions of HSO₄⁻, OH⁻, NO₃⁻, I⁻, Br⁻, Cl⁻, F⁻, CN⁻, ClO₄⁻, HPO₄²⁻ and AcO⁻ at 30 mM. b) Normalized absorbance response of the paper strip.

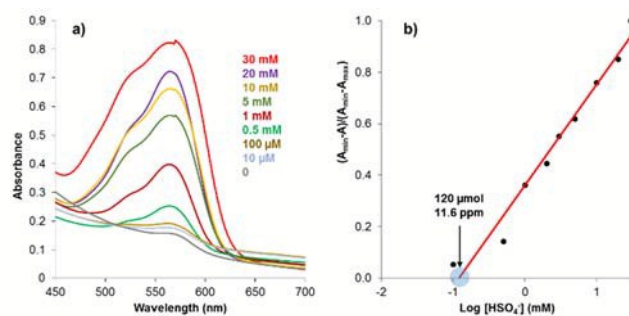


Fig. 6 a) UV-vis absorption spectra of the paper strip various concentration of HSO₄⁻. b) Calibration curve of HSO₄⁻ for the determination of the detection limit.

The spectrophotometric titration experiments were carried out on the paper strip at different concentration of HSO₄⁻ anions (Fig. 6). The absorption band centered at 564 nm becomes more intense upon increasing concentration. Although an increase of the absorption band, with respect to the blank, can be detected at concentration of HSO₄⁻ anions as low as 10 μM, the limit of detection in reproducible condition was calculated with the set of data collected from the titration experiments (Fig. 6b).²⁸ The absorption data collected at 564 nm at various concentrations were normalized between the minimum intensity recorded on the sensor device dipped in HSO₄⁻ free water and the maximum intensity observed at 30 mM. A linear regression curve was fitted to the concentration values 0.5-30 mM of Fig. 6 and a detection limit as low as 120 μmol (corresponding to 11.6 ppm) was determined by extrapolation of the straight line on the ordinate axis. With the objective of limiting the cost of this technology, we assessed the reusability of the paper strip. To this end, we developed a simple methodology allowing several coloration-discoloration cycles for the sensing of different aqueous samples containing HSO₄⁻ anions with the same paper strip. As shown

in Fig. 7a, the deep pink paper, obtained from the sensing of an aqueous sample containing 5 mM HSO_4^- , quickly discolored when dipped in a 1 M NaOH aqueous solution under sonication for 5 minutes. The discolored strip paper turned back to deep pink when exposed again to HSO_4^- anions. This procedure was successfully repeated on four cycles, but the fragility of the paper strip might limit the number of successive reuses to get reliable results.

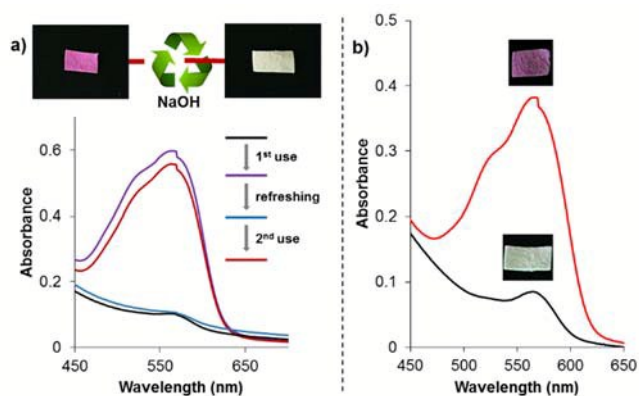


Fig. 7 a) UV-vis absorption spectra of the paper strip upon two successive reuses. As inset, pictures of the paper strip dipped in a solution of HSO_4^- anions (left) and refreshed in a solution of 1 M NaOH (right). b) UV-vis absorption spectrum of the paper strip dipped into an aqueous solution containing NO_3^- , I^- , Br^- , Cl^- , ClO_4^- anions at 5 mM, with (red line) and without HSO_4^- (black line) with a photograph of the paper as inset.

With the objective of developing an analytical device working in real situation, we analyzed two aqueous samples containing a cocktail of anions. In the first sample, NO_3^- , I^- , Br^- , Cl^- , and ClO_4^- anions were mixed at 5 mM in water, while the same cocktail was used for the second sample but with the additional presence of HSO_4^- anions. As it can be seen on the UV-vis absorption spectra of the paper strip dipped in these solutions, the analytical device was not sensitive to a cocktail of anions in the absence of HSO_4^- (Fig. 7b). Conversely, both the coloration and the UV-vis responses of HSO_4^- were not affected by the presence of other anions, demonstrating the absence of interference and the high selectivity of the device.

In summary, we developed the first hydrogen sulfate-sensitive solid-state sensor working in water through colorimetric and optical detection. The smart device fabricated by grafting a rhodamine-modified sensor onto the highly hydrophilic surface of paper, allows on-site analysis of aqueous samples and does not require skilled operator for the colorimetric detection. The high selectivity of the device for HSO_4^- anions, even in the presence of other amphiphilic anions, is the result of the unique combination of hydrogen bond receptor and donor sites in the opened form of rhodamine. This practical technology should find broad applications in environmental and analytical sciences. We are currently working on the diversification of this technology to the sensing of other liquid and gas analytes.

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Notes and references

- H. Li, J. Fan and X. Peng, *Chem. Soc. Rev.*, 2013, **42**, 7943-7962.
- K. P. Carter, A. M. Young and A. E. Palmer, *Chem. Rev.*, 2014, **114**, 4564-4601.
- X. H. Li, X. H. Gao, W. Shi and H. M. Ma, *Chem. Rev.*, 2014, **114**, 590-659.
- P. Mahato, S. Saha, P. Das, H. Agarwalla and A. Das, *RSC Adv.*, 2014, **4**, 36140-36174.
- R. Saini, N. Kaur and S. Kumar, *Tetrahedron*, 2014, **70**, 4285-4307.
- P. A. Gale and C. Caltagirone, *Chem. Soc. Rev.*, 2015, **44**, 4212-4227.
- S. Lee, K. K. Y. Yuen, K. A. Jolliffe and J. Yoon, *Chem. Soc. Rev.*, 2015, **44**, 1749-1762.
- F. Wang, L. Wang, X. Q. Chen and J. Y. Yoon, *Chem. Soc. Rev.*, 2014, **43**, 4312-4324.
- F. Si, C. E. Romero, Z. Yao, Z. Xu, R. L. Morey and B. N. Liebowitz, *Fuel Process. Technol.*, 2009, **90**, 56-66.
- I. J. L. Sessler, E. Katayev, G. D. Pantos and Y. A. Ustynuk, *Chem. Commun.*, 2004, 1276-1277.
- I. R. Shen, X. Pan, H. Wang, J. Wu and N. Tang, *Inorg. Chem. Commun.*, 2008, **11**, 318-322.
- I. R. Shen, X. Pan, H. Wang, L. Yao, J. Wu and N. Tang, *Dalton Trans.*, 2008, 3574-3581.
- S. Samanta, P. K. Samanta, S. Dutta and P. Biswas, *Spectrochim. Acta, Part A*, 2015, **147**, 262-269.
- L.-L. Zhou, H. Sun, H.-P. Li, H. Wang, X.-H. Zhang, S.-K. Wu and S.-T. Lee, *Org. Lett.*, 2004, **6**, 1071-1074.
- X. He, S. Hu, K. Liu, Y. Guo, J. Xu and S. Shao, *Org. Lett.*, 2006, **8**, 333-336.
- H. J. Kim, S. Bhuniya, R. K. Mahajan, R. Puri, H. Liu, K. C. Ko, J. Y. Lee and J. S. Kim, *Chem. Commun.*, 2009, 7128-7130.
- M. Alfonso, A. Tárraga and P. Molina, *Org. Lett.*, 2011, **13**, 6432-6435.
- A. Mallick, T. Katayama, Y. Ishibasi, M. Yasuda and H. Miyasaka, *Analyst*, 2011, **136**, 275-277.
- W. Xue, L. Li, Q. Li and A. Wu, *Talanta*, 2012, **88**, 734-738.
- S.-T. Yang, D.-J. Liao, S.-J. Chen, C.-H. Hu and A.-T. Wu, *Analyst*, 2012, **137**, 1553-1555.
- P. Kaur, H. Kaur and K. Singh, *Analyst*, 2013, **138**, 425-428.
- A. S. Goldmann, T. Tischer, L. Barner, M. Bruns and C. Barner-Kowollik, *Biomacromolecules*, 2011, **12**, 1137-1145.
- C. Kaewtong, B. Wannoo, Y. Uppa, N. Morakot, B. Pulpoka and T. Tuntulani, *Dalton Trans.*, 2011, **40**, 12578-12583.
- A. Hakonen, J. E. Beves and N. Stromberg, *Analyst*, 2014, **139**, 3524-3527.
- H. I. A. S. Gomes and M. G. F. Sales, *Biosens. Bioelectron.*, 2015, **65**, 54-61.
- A. Reisch, P. Didier, L. Richert, S. Oncul, Y. Arntz, Y. Mély and A. S. Klymchenko, *Nat. Commun.*, 2014, **5**, 4089.
- C. Tan and Q. Wang, *Inorg. Chem.*, 2011, **50**, 2953-2956.
- M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414-1418.