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Gas Sensitivity of Blends of Metalloporphyrins and Colorimetric Acid-Base Indicators

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Abstract

Optical methods combine the wide availability of molecular indicators with simple and contactless measurements. In this context, indicator-displacement assay is a viable strategy for developing optical chemosensors with synthetic receptors. Such approach may be used to overcome the limits of sensing molecules and to widen the range of detectable compounds. In this paper, it is shown that proper blends of porphyrins and Lewis acid-base indicators can give rise to sensitive units whose properties exceed those of single components.

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1. Introduction

Porphyrins are among the most interesting molecules for opto-chemical sensors; in these molecules the interaction with analytes can elicit a great variation of the optical properties such as absorbance and emission. However, only a subset of the interactions occurring between analytes and metalloporphyrins is actually measurable with optical transducers. An interesting method to extend the selectivity range of the metalloporphyrins based optical sensors is offered by the indicator displacement assay (IDA) [1]. In IDA a chemical receptor is bound to a colorimetric indicator whose displacement occurring upon the interaction with analytes gives rise to a readable optical signal. IDA enlarges the capabilities of optical sensors, allowing for instance for the development of saccharides sensitive fluorescent assays [2]. In this

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paper, a blend of one porphyrin and one Lewis acid-base indicator is used to prepare sensing layers. The strategy in this case somehow differs from the previously proposed IDA, because both the components are endowed with colored features and sensing capabilities. The change of the optical properties of single dyes and their mixture was measured with a computer screen photoassisted technology (CSPT) setup. According to this technique a computer screen programmed to display colors is used as a light source and a webcam is used as a detector. Such an arrangement was demonstrated to be sufficiently sensitive to capture changes occurring in porphyrins exposed to vapors [3, 4]. The mixture of porphyrin and indicator, indeed, shows an enhanced sensitivity with respect to that of the mixture components.

2. Experimental

Four tetraphenylporphyrins (H_2TPP , $MnTPP$, $ZnTPP$, and $RuTPP$) were blended with two Lewis acid-base indicators: nile blue (NB) and bromocresol purple (BCP). The blends were further mixed with a standard polymeric matrix based on plasticized polyvinylchloride (composition: 1% wt dye, 33% wt PVC, 66% wt plasticizer) in order to prepare a solution that can be deposited as a solid layer. A plastic substrate was coated with an array of spots of pure constituents and porphyrin-indicator blends. The sensing layers were placed in a sealed measurement cell and illuminated with a computer screen displaying pure colors (red, green and blue). Images were acquired in transmission mode by a webcam, as schematically represented in Fig. 1a. The appearance of the sensing layers as illuminated with white light is shown in Fig 1b.. Sensitive layer was exposed to concentrations of butanol, acetic acid, toluene, hexane, trimethylamine, and triethylamine. The response of each spot to the exposure was calculated as the difference between the camera signals taken before and during the exposure to gas. The total response of the spot is calculated considering the camera intensity for all the pixels in the same spot processed with an algorithm aimed at removing common modes due to camera and screen non homogeneities [4]. For the scopes of this abstract only the case of green light illumination and green camera channel is illustrated.

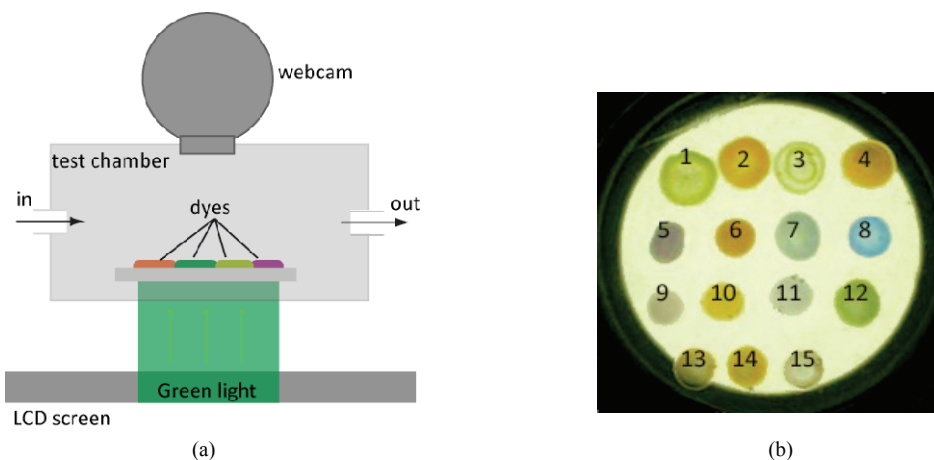


Fig. 1. (a) Measurement setup follows the standard CSPT arrangement illustrated under green illumination; (b) Sensitive layers spotted on a plastic substrate and imaged by the camera under white illumination. Pure porphyrins: 1: $MnTPP$; 5 $ZnTPP$; 9: H_2TPP ; 13: $RuTPP$. Pure indicators: 4: BCP 8: NB. Each line contains the blends porphyrin-indicator. Spot 12 is a blend BCP-NB.

3. Results

For some blends, absorbance spectra indicate that an interaction between indicators and porphyrin occurs. In these cases, the optical spectrum differs with respect to the sum of porphyrin and indicator spectra (Fig. 2). The difference is found in particular for MnTPP blends. As interaction evidence, the Soret band appears blue-shifted of about 10 nm in the case of BCP and about 5 nm in the mixture with Nile Blue.

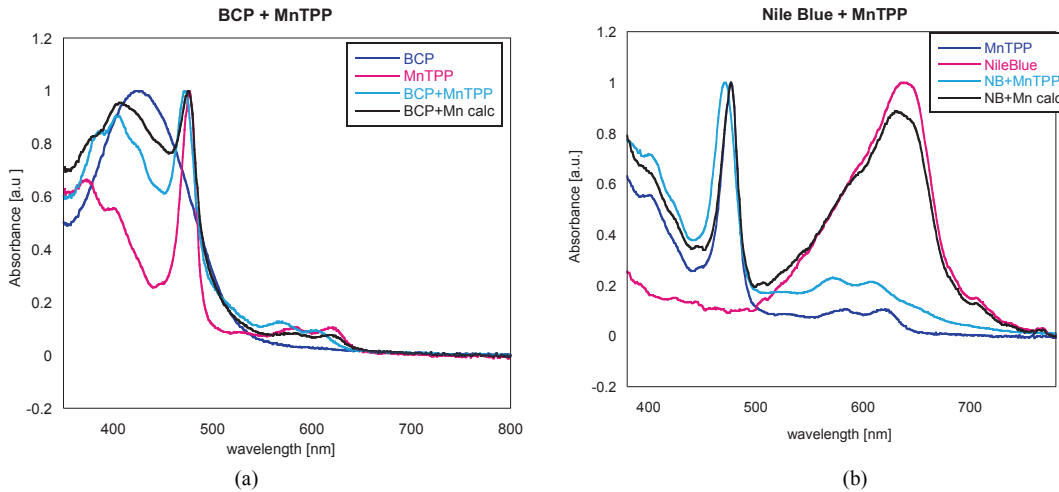


Fig. 2. Absorbance spectra of (a) MnTPP-BCP and (b) MnTPP-NB blends and single components compared with the spectra calculated as the weighted sum of pure porphyrin and indicator spectra.

It is then supposed that vapours can either displace the indicator from the porphyrin or “disturb”, in a 3 bodies interaction, the molecular equilibrium. This effect is particularly evident for hexane; a compound that cannot change the optical spectrum of porphyrins, it elicits a not negligible response in both MnTPP-BCP and MnTPP-NB blends (Fig. 3a).

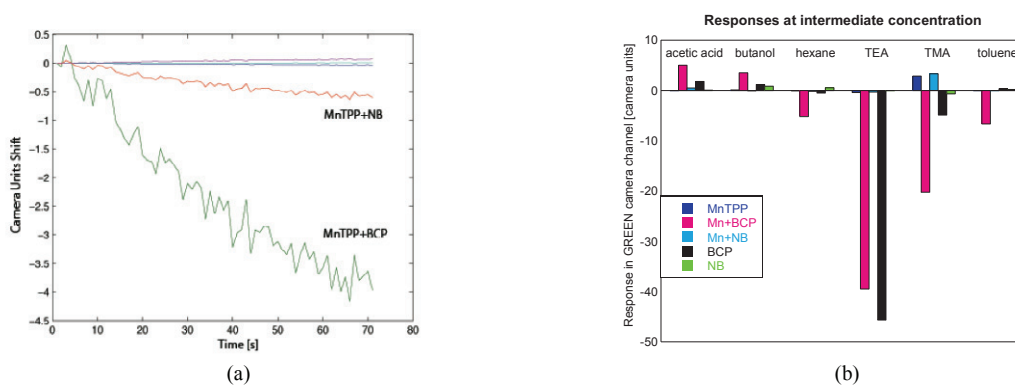


Fig. 3. (a) Response of all spots to 5000 ppm of hexane (3% of saturation pressure). Only blends of MnTPP and the two indicators show a readable signal. (b) Comparison of the responses of indicators, pure MnTPP and blends. The response is expressed as the camera units shift averaged for all the pixels of the spot.

A comparison among the responses of MnTPP blends and single components for all the test compounds is shown in Fig. 3b. The MnTPP-BCP blend evidences a response also for toluene, acetic acid and hexane, whereas the single components show a negligible signal.

In Fig. 4 the sensitivities of all spots for all tested compounds are reported. For each spot and each vapor the sensitivity was calculated as the slope of the linear regression of the camera units shift versus vapour concentration. For sake of clarity, in Fig. 4 the sensitivities are classified in three groups: large positive sensitivity, large negative sensitivity, and negligible sensitivity. The threshold for large sensitivity has been arbitrarily fixed at 10^{-3} camera units/ppm in absolute value. As expected, strong Lewis electron donors (such as amines) elicit large changes (either positive or negative) in almost all the spots, for the other vapours the sensitivity is rather sparse as required for sensor array applications.

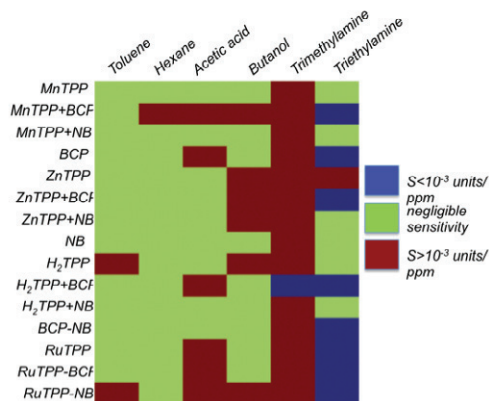


Fig. 4: Grouped sensitivity map.

3. Conclusions

In this paper we show that a proper blend of porphyrin and pH indicator exceeds the sensing properties of single components, allowing for the detection of compounds that were not detectable by optical transduction. Interestingly, the sensitivity to vapors is rather dispersed, favoring the development of sensor arrays. Most of the blends porphyrins-indicators behave differently from the single components giving a demonstration of the accomplishment of the IDA strategy.

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