

Towards Metal-Organic Framework based Optical Sensors for Pesticides Detection

Alba Finelli¹, Pierrick Clément¹, Xavier Lefèvre¹, Alexandra Beard¹, Raphaël Pugin¹
¹ CSEM, Rue Jaquet-Droz 1, 2002 Neuchâtel, Switzerland

Alba.finelli@csem.ch

Summary:

Organophosphates are extensively employed as pesticides in intensive agriculture. Being strong nerve agents, they represent one of the most common causes of poisoning in the world. Given their detrimental impact on both human health and the ecosystem, it is critical to develop a compact, reliable, fast, selective, and low-cost sensor able to detect pesticides residues in aqueous medium such as drinking water, foods, and soil samples.

Keywords: Metal organic frameworks, Optical sensor, Nitro compounds, Pesticides, Sensing layer

Introduction

Exhibiting a high surface area, metal-organic frameworks (MOFs) can be customized to effectively adsorb the targeted analytes. Interest in integrating such porous materials as selective adsorbent layers in chemical sensors has increased lately [1]. Though, refinement of sensing materials and transducer mechanisms is still essential to increase the reliability, selectivity, and response kinetics to a level suitable for commercial purposes. While MOFs seem excellent candidates for selective sensing, several studies demonstrate a higher response for the selected analyte compared to interferents because the compounds are tested each independently. In real-world applications, the sensor will be exposed to all components concurrently, including some interferents present at much higher concentrations than the analyte. One way to address the selectivity challenge is to combine cross-sensitive sensors to form an array or "electronic nose" (e-nose) [2].

When the combined response of the array contains enough non-correlated information, the focused analyte can be monitored in a complex environment via chemometric data analysis (Figure 1).

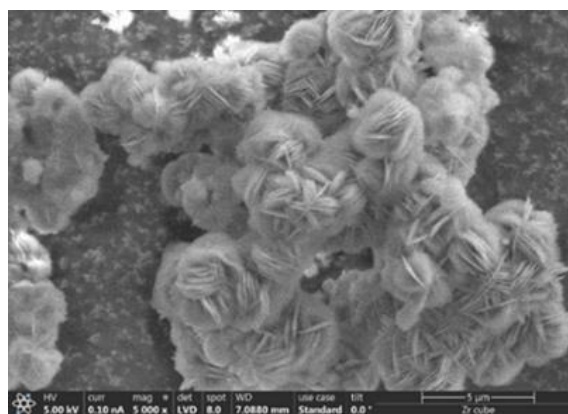


Fig. 2. Scanning electron micrograph of ursin-like Zr-MOF.

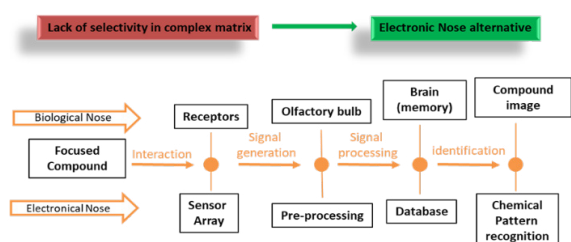


Fig. 1. E-nose concept schema.

Results

Due to the variety of organophosphate pesticides, nitro-based compounds have been focused on this study. Luminescent Zr-MOFs have been synthesized for the specific uptake of the toxic analytes from 1,2,4,5-tetrakis(4-carboxyphenyl) benzene and Zr(IV)[3]. Characterization by X-ray diffraction (PXRD) and SEM (Figure 2) shows an ursin-like morphology. Due to the luminescence properties of the MOF, the first sensing tests have been done by fluorimetry. Together with a surface area corresponding

to 1453.2 m²/g and micropores size of about 0.60 nm, this MOF has shown a specific affinity with nitro-based family by the quenching of the luminescence of the fluorophore via adsorption. Zr-MOF has been tested in the presence of other compounds containing a nitro group as well as nitrates and nitrites salts (Figure 3). It can be observed that all compounds containing a nitro group extinguish the fluorescence to varying degrees. The most probable explanation is that the presence of the -NO₂ group has caused the transfer of photoexcited electrons from the Zr-MOF to the nitro compounds. Therefore, the quenching of the MOF will strongly depend on the electro-attractive properties of the nitro compound. We could then observe a lack of selectivity of this MOF when targeting a specific compound, but it appears to be reactive to most nitro compounds.



Fig. 3. Photoluminescence responses of Zr-MOF against 10 organophosphates compounds containing nitro group. The final concentration of all the compounds is 0.012 mM.

The interesting luminescent properties of Zr-MOF have been utilized to create an active layer for detecting pollutant compounds containing a nitro group. For this purpose, the MOF was incorporated into a silica-based sol-gel. This compound can then be deposited onto a transparent surface such as PET via spin, bar, or spray coating (Figure 4). The coated layer has shown to be sufficiently hydrophilic to enable a rapid response to the presence of this family of pollutants. Further characterizations are now ongoing to evaluate and confirm the

reliability, selectivity, and sensitivity of the final sensor.

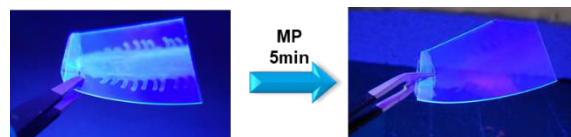


Fig. 4. MOF-based coating quenched off by the presence of methyl parathion (MP) after 5 minutes.

Conclusion

To conclude, we acknowledge that the selectivity of MOFs can be a significant limitation for the development of an optimal sensor especially for real-world applications. To tackle this primary challenge, the design of an electronic e-nose concept could be developed using the remarkable properties of MOFs for the detection of pollutant families. By integrating multiple MOF-based sensors with cross-sensitivity, we could effectively identify compounds within the same family.

References

- [1] Furukawa H, Cordova KE, O'Keeffe M, Yaghi OM. The chemistry and applications of metal-organic frameworks. *Science* 30 (2013) 341
- [2] Freund R., et al. "The Current Status of MOF and COF Applications." *Angewandte Chemie International Edition* (2021)
- [3] He, K., Li, Z., Wang, L., Fu, Y., Quan, H., Li, Y., ... & Xu, X. A water-stable luminescent metal-organic framework for rapid and visible sensing of organophosphorus pesticides. *ACS applied materials & interfaces* 11 (2019) 26250