

A Metalloporphyrin-Based Colorimetric Nose: "Smell-Seeing"

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Array-based vapor sensing has emerged as a powerful approach toward the detection of chemically diverse analytes. Based on cross-responsive sensor elements, rather than receptors for specific species, these systems produce composite responses unique to an odorant, in a fashion similar to the mammalian olfactory system.^{1,2} Previous electronic noses employing conductive polymers and polymer composites,^{3,4} fluorescent dye/polymer systems,^{5,6} tin oxide sensors,⁷ and polymer-coated surface acoustic wave (SAW) devices⁸ have relied primarily on weak chemical interactions (e.g., physical adsorption) for detection. While these approaches have demonstrated success in chemical vapor detection and differentiation, their primary aim has been the detection of non-coordinating organic vapors. Array detection of metal-binding species, such as amines, phosphines, and thiols, has been relatively unexplored.

Metalloporphyrins are a natural choice for the detection of metal-ligating vapors because of their open coordination sites for axial ligation, their large spectral shifts upon ligand binding, and their intense coloration. We have achieved colorimetric detection of a wide range of odorants using an array of metalloporphyrins as vapor-sensing dyes immobilized on reverse phase silica gel.^{9,10} By simply subtracting digital images of the array before and after exposure, qualitative color fingerprints can be obtained for a given analyte. As shown in Figure 1 below, the color change patterns provide striking visual identification for a range of ligating vapors (including alcohols, amines, phosphines,

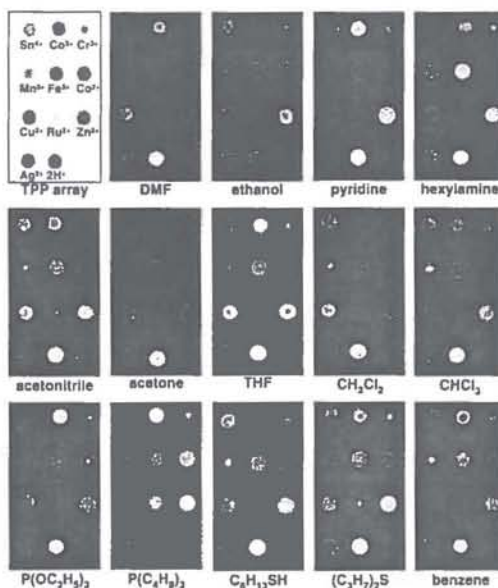


Figure 1. Color change fingerprints (shown in black and white) for a series of organic vapors at saturation vapor pressure.

phosphites, thioethers, and thiols). Weakly-ligating vapors such as arenes, halocarbons, and ketones can also be differentiated. Diffuse reflectance spectroscopy studies have shown that solid-state spectral shifts are similar to those known for ligation in solution.

The array has demonstrated interpretable and reversible responses even to mixtures of strong ligands, such as pyridines and phosphites. Color change patterns for mixtures of 2-methylpyridine and trimethylphosphite were shown to be distinct from responses to either of the neat vapors. Good reversibility was demonstrated for this mixture upon cycling between the neat analyte extremes. Monotonic color changes upon exposure to increasing concentrations of a given analyte allowed for quantitative analysis. Responses at analyte concentrations as low as 35 ppb have been observed; a wide range of species can be distinguished at hundreds of ppb. Notably, the metalloporphyrin array showed no susceptibility to water vapor; analyte detection was possible even in the presence of a large water background. This represents a key advantage over almost all existing electronic nose technologies, which suffer from sensitivity to changes in water vapor concentration.

To improve response times, the “smell-seeing” array was miniaturized. Miniaturization was necessary to avoid slow equilibration times at low ppm levels due to the high surface area of the reverse phase silica support. Deposition of plasticized porphyrin-polymer films on Teflon posts (Figure 2) resulted in faster response times (~21-fold) than with reverse phase silica at low analyte levels.

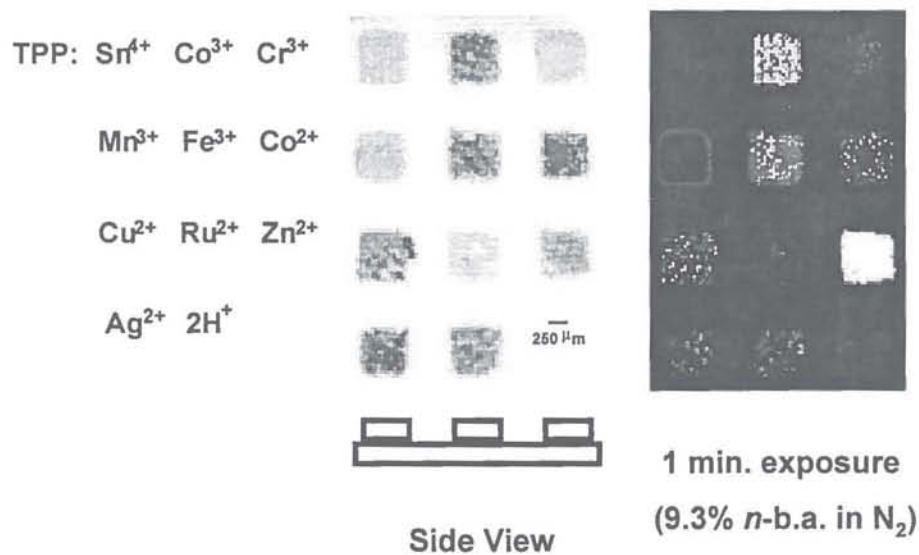


Figure 2. Deposition of plasticized metalloporphyrin/polymer films on a Teflon micropostplate. Response to saturated *n*-butylamine is shown (in black and white).

Chemometric statistical tools have been used to study the porphyrin array responses. Principal component analysis (PCA) revealed that the porphyrin array responses are relatively specific, having a low degree of redundancy. Furthermore, almost all of the chosen metalloporphyrins contributed to analyte distinction, meaning the initial array was well-chosen for the vapor sensing task. Hierarchical cluster analysis (HCA) was used to quantitatively compare vapor fingerprints. HCA analysis revealed distinction of all of the tested vapors, with groupings formed among similar analytes, such as phosphorus-containing ligands, sulfur-based ligands, and nitrogenous bases.

While libraries based on metal center variation allowed for differentiation by analyte class (i.e., amine vs. alcohol vs. phosphine, etc.), arrays of metalloporphyrins with sterically hindered binding sites allowed for intrafunctional distinction (i.e. *n*-butylamine vs. cyclohexylamine). Such differentiation has been demonstrated with a family of bis-pocketed zinc siloxyl-porphyrins.¹¹ Use of solvatochromic and pH-sensitive dyes in an expanded dye array allowed for the detection of Lewis acid analytes.

Medical diagnostics, food and beverage quality control, workplace toxin monitoring, and warfare agent detection are all areas which could potentially benefit from the “smell-seeing” technique. We have developed a “smell camera” prototype that couples a miniaturized metalloporphyrin array with a digital camera for imaging. This format provides a portable version of the invention for the mentioned applications, many of which are currently under investigation.

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