One- and Two-Photon Fluorescent Polyhedral Oligosilsesquioxane (POSS) Nanosensor Arrays for the Remote Detection of Analytes in Clouds, in Solution, and on Surfaces

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A series of polyhedral oligosilsesquioxane (POSS) nanosensors functionalized with fluorophores that change their wavelength of emission in response to their chemical environment has been synthesized and characterized by IR, NMR, UV, one- and two-dimensional fluorescence spectroscopy, MALDI-TOF MS, and electrospray MS. When each nanosensor in an array of *n* nanosensors is functionalized with a different wavelength shifting fluorophore, the array can generate a unique fingerprint comprised of *n* emission wavelength data points in response to a given chemical warfare agent (CWA) simulant or toxic industrial chemical (TIC). One-photon fluorescence fingerprints were constructed by measuring the fluorescence spectra of nanosensor−analyte pairs in solution. Two-photon fluorescence fingerprints were then generated by remotely interrogating nanosensor−analyte pairs using a femtosecond IR laser and a stand-off fluorimeter. Two-photon fingerprints were obtained for analytes in solution, on a surface, and in cloud form. A four-component nanosensor array could differentiate a homologous series of alcohols and distinguish G and VX classes of nerve agent simulants.

Introduction

At the most general level, stand-off sensing techniques must function either by passive detection of waves emitted from remote objects (e.g., passive FTIR), or by actively sending a wave to a remote object, and obtaining information by analyzing the wave(s) returning from the object (e.g., laser detection and ranging, LIDAR). An early report[1] on the topic of stand-off detection of air pollutants correctly foresaw that the major technical obstacles in remote detection would be scattering caused by solid particles or droplets and measurement of low-energy signals against a complex and constantly changing background. This challenge has traditionally been addressed by modifying the detection system and designing ever more powerful and sophisticated instrumentation and data processing algorithims.[2–4] However, an alternative strategy is to modify the remote location itself, such that the location is able to send higher-quality information back to the sensor. For example, enhanced Raman spectroscopy has been developed where colloidal silver or gold nanoparticles have been sprayed onto a surface to improve the quality of the signal it generates, and the surface has been remotely interrogated using a Raman telescope at a distance of 5 meters.[5] Another way to enhance the quality of information arriving from the remote location is to introduce fluorophoric nanoparticles at the remote location and use the nanoparticles to generate fluorescence signals that give information about the chemical composition of their immediate vicinity.

In this study, a set of polyhedral oligosilsesquioxane (POSS) nanosensors designed to change their wavelength of fluorescence emission upon interaction with analytes was synthesized and characterized (Figure 1). A four-component array of nanosensors was used to generate fluorescence data sets (fingerprints) for a number of analytes including chemical warfare agent (CWA) simulants and toxic industrial chemicals (TICs) by measuring the one-photon fluorescence spectra of nanosensor−analyte pairs. The feasibility of using the nanosensor array for the remote detection of analytes in clouds and on surfaces was then evaluated. A femtosecond laser was used to interrogate the array and induce two-photon fluorescence in the nanosensors, and a remote fluorescence probe was used to record the responses of the nanosensors.

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