PROTECTION - SCIENCE AND TECHNOLOGY ADVANCES FOR CHEMICAL AND BIOLOGICAL PROTECTION

Metal–organic Framework/textile Composites For The Rapid And Sensitive Assessment Of Exposure To A Toxic Organophosphonate

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A timely and ready detection of exposure of warfighters to toxic substances is essential to facilitate an adequate (medical) response. However, the detection of low levels of low-volatile toxic chemicals dispersed in the air as an aerosol or deposited on a surface is a considerable challenge for conventional detection equipment, especially with low-volatile agents. We developed a metal-organic framework (MOF) that rapidly changes color when exposed to a non-volatile nerve agent. MOFs are crystalline solids comprised of metal clusters coordinated by organic linkers to form porous networks. These materials have shown promise in the catalytic degradation of toxic organophosphonates in recent years, and are currently being researched for applications to protective clothing. In this work, a Zr-containing MOF that is well-known as an effective catalyst (MOF-808), was post-synthetically modified with ditopic 5,5-dithiobis(2-nitrobenzoic acid) (DTNB), a bidentate reactive dye. According to the crystal structure as well as DFT calculations, the two carboxylic acids in DTNB bridge two adjacent Zr clusters in MOF-808. In the presence of an organophosphonate, Zr-OH sites on the MOF rapidly hydrolyze the agent followed by reaction of one of the degradation products with the MOF-bound DTNB, resulting in a change of color of the crystals from white to bright orange. Immobilization of the crystals on textile enabled its application as a wipe for the rapid and sensitive assessment of surfaces for the presence of agent. Moreover, exposure of the textile to a low amount of aerosolized organophosphonate resulted in rapid discoloration of the textile, suggesting that its use as a wearable indicator of exposure to this compound is feasible. The latter feature was tested using a setup, designed and built in-house, that we call the Chemical Hot Aerosol Research Tool (CHART), in which we are capable of generating highly defined (concentration, size distribution) toxic aerosols for a variety of purposes. We anticipate that the detoxifying activity of the textile as well as the availability of the CHART setup will boost the development and evaluation of protective materials with a self-cleaning capacity towards toxic aerosols.

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