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Mof a Unique Topological Architecture for Detection of Total Organophosphate Pesticides

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Abstract

Metal organic frameworks (MOFs) are advanced class of supra-molecular hybrid network built from metal ions and organic bridging ligands with well-defined coordination geometry. Despite of various exclusive properties, MOF has less conductivity attributed by the organic linker molecules which is making it unsuitable to act as an efficient electrochemical sensing bed. In the present investigation, chemically synthesized MOF 5 was modified either by integrating with anisotropic gold Nano-rod (AuNR) or gold nano-particle (AuNP) tagged receptor biomolecule (IgG) to lower down over all resistance of the sensor. Spin coated MOF 5 on indium tin oxide coated (ITO) electrode was decorated with electrochemically deposited anisotropic gold Nano rod (AuNR) and later functionalized with esterase enzyme to fabricate electrochemical enzymatic sensor [AchE (acetylcholinesterase)/Cys (cysteamine)/AuNR/ MOF/ITO] for sensing of Op and carbamates. The synthesized AuNPIgG nano bio hybrid was immobilized on spin coated MOF 5 on ITO electrode to develop immunosensor [BSA (bovine serum albumin)/AuNP-IgG/MOF 5/ITO] for ultra-low sensing of total Op. The modulation of current value with change in pesticide (chloropyrofos) concentration shows a broad dynamic range of 0.03-0.6 ppb with linearity ($R2=0.91$) and a sensitivity of 2.04 µA ppb-1cm-2. In the second case, the interaction between Op and AuNP- IgG is due to antigen and antibody interaction enhances the conductivity of the electrode developed and causes a gradual increase in current with increase in concentration of Op (chloropyrofos) and demonstrates a dynamic range of 0.004 ppb to 0.1 ppb and a sensitivity of 0.0254 µA ppb-1cm-2. Interference study in presence of heavy metal ions including Ni2+, Cu2+, Zn2+, Pb2+, reveals that minimum interference is observed by both electrodes excluding Ni2+ showing an interference of 23.86 % for immunosensor. Both the electrodes are stable up to 30 days. Both the sensors are successfully exploited to determine the total Op levels in mixture of various Op and spiked vegetable extract. However, the enzymatic sensors also showed satisfactory results when exhaustively used to detect Op in the field sample at a regular interval. In future, MOF-mono clonal antibody conjugate will be explored for specific detection parathion, methyl parathion and paraoxonon etc.

Organophosphates (also known as phosphate esters, or OPEs) are a class of organ phosphorus compounds with the general structure O=P They can be considered as esters of phosphoric acid. Like most functional groups organophosphates occur in a diverse range of forms, with important examples including key biomolecules such as DNA, RNA and ATP, as well as many insecticides, herbicides, nerve agents and flame retardants. Today, organophosphates make up about 50% of the killing agents in chemical pesticides

Organophosphate pesticides (OPPs), like some nerve agents, inhibit acetyl cholinesterase, which is broadly essential for normal function in insects, but also in humans and many other animals. OPPs affect this enzyme in varied ways, a principle one being through irreversible covalent inhibition, and so create potentials for poisoning that vary in degree. The brain sends out neurotransmitters to the nerve endings in the body; organophosphates disrupt this process from occurring. This chemical, organophosphate works by disrupting the enzyme acetyl cholinesterase. Acetyl cholinesterase breaks down the acetylcholine neurotransmitter, which sends out signals to other nerve endings in the body.

For instance, parathion, one of the first OPPs commercialized, is many times more potent[clarification needed] than marathon, an insecticide used in combating the Mediterranean fruit fly (Med-fly) and West Nile virus-transmitting mosquitoes.[4] Human and animal exposure to them can be through ingestion of foods containing them, or via absorption through the skin or lungs.

The human and animal toxicity of OPPs make them a societal health and environmental concern; the EPA banned most residential uses of organophosphates in 2001, but their agricultural use, as pesticides on fruits and vegetables, is still permitted, as is their use in mosquito abatement in public spaces such as parks. For instance, the most commonly used OPP in the U.S., malathion, sees wide application in agriculture, residential landscaping, and pest control programs (including mosquito control in public recreation areas). As of 2010, forty such OPPs were registered for use in the U.S. with at least 73 million pounds used in one time period[which?] in agricultural and residential settings.

Commonly used organophosphates have included:

- Parathion
- malathion
- methylparathion
- chlorpyrifos
- diazinon
- dichlorvos

Studies have shown that prolonged exposure to OPPs in the case of farm workers—can lead to health problems, including increased risks for cardiovascular and respiratory disease, and cancer. In the case of pregnant women, exposure can result in premature births. In addition, permanent damage to the brain’s chemical make-up and changes in human behaviour and emotion can occur to the foetus in pregnant women.

Organophosphate pesticides degrade rapidly by hydrolysis on exposure to sunlight, air, and soil, although small amounts can be detected in food and drinking water.[citation needed] Organophosphates contaminate drinking water by moving through the soil to the ground water. When the pesticide degrades, it is broken down into several chemicals. Organophosphates degrade faster than the organ chlorides.[citation needed] The greater acute toxicity of OPPs results in the elevated risk associated with this class of compounds.

Many "organophosphates" are potent nerve agents, functioning by inhibiting the action of acetyl cholinesterase (Ache) in nerve cells. They are one of the most common causes of poisoning worldwide, and are frequently intentionally used in suicides in agricultural areas. Organophosphate pesticides can be absorbed by all routes, including inhalation, ingestion, and dermal absorption. Their inhibitory effects on the acetyl cholinesterase enzyme lead to a pathological excess of acetylcholine in the body. Their toxicity is not limited to the acute phase, however, and chronic effects have long been noted. Neurotransmitters such as acetylcholine (which is affected by organophosphate pesticides) are profoundly important in the brain's development, and many organophosphates have neurotoxic effects on developing organisms, even from low levels of exposure. Other organophosphates are not toxic, yet their main metabolites, such as their oxons, are. Treatment includes both a pralidoxime binder and an anticholinergic such as atropine.

Biography

Tinku Basu is the Deputy Director in Amity Institute of Nanotechnology. She had pursued her PhD from IIT, Kharagpur. She has 50 national and international publications. She has filed 12 complete patents. Her area of research is biosensors, polymer science and technology, functionalization of Nano materials, metal organic frame work, self-assembly and Nano composites etc.