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Practical utilization of nanocrystal metal organic framework biosensor for parathion specific recognition

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ABSTRACT

The feasibility of the nanocrystal metal organic framework $[Cd(atc)(H_2O)_2]_n$ (NMOF**1**) as a biosensor is explored for the specific recognition of parathion. The luminescence properties of the NMOF**1**/antiparathion complex were tested for the detection of parathion. Because of the fluorescent properties, the anti-parathion antibody interacted with parathion in order to facilitate its detection at a dynamic concentration range from 1 ppb to 1 ppm. The assay was validated against some environmental samples by gas chromatography with solid phase extraction (SPE). Accordingly, the NMOF biosensor tested in this work is demonstrated as parathion-specific with high surface loading and high sensitivity.

1. Introduction

Over the past several decades, metal organic frameworks (MOFs) have been introduced as new and interesting crystalline-porous materials for diverse applications in the sensing of small molecules, solvents, and explosives [1–9]. At present, many research groups around the world are focusing on the practical utilization of MOFs. As part of such efforts, our group has been investigating the applicability of MOFs for the detection of organophosphate pesticides (OPs) [7–11]. Two applied approaches, i.e., direct chemo-sensing and immune-sensing, have been recognized as one of the most promising tools for their detection (Table 1).

The chemosensing approach with MOF-5 ($Zn_4O(BDC)_3$ (BDC = 1,4-benzenedicarboxylate) and NMOF**1** ($[Cd(atc)(H_2O)_2]_n$, H_2atc (2-aminoterephthalic acid)) provided the robust and sensitive optical detection of the OPs containing nitro family — namely, parathion, methyl parathion, paraoxon, and fenitrothion [12,13]. Both MOF-5 and NMOF**1** have been recommended as the direct chemosensing tool for such OPs at detection limits of 1 to 5 ppb range. However, selective solid phase extraction steps were suggested, prior to the analysis in order to avoid the interference from other $–NO_2$ compounds present in the sample [12,13]. On the other hand, immunosensing of parathion with electrochemical techniques enables the specific detection of purely parathion on the surface of MOFs through both direct sensing and biosensing (grafting of biomolecules, i.e., a specific antibody) [14–16].

Immobilization experiments have also been pointed out as the utility tool of the MOF/antibody complex for immunohisto-fluorescence based applications for quantitative detection of counterantigen with the subppm sensitivity [14–16]. In a very recent study, the grafting of biomolecules was performed on NMOF**1** via activation of the pendant –COOH group of the organic linker using EDC [(1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide [15,17]. The activated NMOF**1** was incubated with an antibody to form a biosensing substrate. These NMOF**1**-antibody complexes then provided better detection results due to improved stability, dispersibility, and yield in aqueous phase [15,17]. Electrochemical impedance spectroscopic (EIS)-based sensing was also carried out to improve the detection of parathion using an anti-parathion functionalized conducting NMOF**1** layer [17].

In this research, in order to achieve the practical applications of the NMOF**1**-based immunosensor (with considerably improved sensor sensitivity or low detection limit), its biofunctionalization properties have been investigated to develop a simple and fast optical biosensor for the detection of parathion. Importantly, NMOF**1** have been offered well dispersive nature in water due to which sufficiently high fluorescent intensity retaining with a distinct particle appearance even after their conjugation with anti-parathion antibody. Therefore, photoluminescence response of NMOF**1**/anti-parathion probe to

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Table 1
Recently reported MOFs based pesticide sensing with lower detection limit.

MOFs	**Detection method**	**Target analytes**	Detection limits	**Samples**	**Ref.**
B-MOF	Electrochemical sensing	Methyl parathion	6 ppb	Organic solvent	[10]
MOF-5	Chemosensing	NO_2 OPs (methyl parathion, parathion, paraoxon and fenitrothion)	5 ppb	Organic solvent	[12]
NMOF**1**	Chemosensing	do	1 ppb	Organic solvent	[13]
NMOF**1** (LBL)	Impedimetric sensing	Parathion	0.1 ppb	Water and rice	[18]

recognize parathion showed the excellent fluorescent properties. Most importantly, this study is thus expected to ensure that NMOF**1**-based biosensing is feasible enough for detecting OPs. As such, this approach is likely to offer us to draw a roadmap for expanding its applicability toward the diverse industrial outputs.

2. Materials and methods

Herein, synthesis and pendant group activation of NMOF**1** were carried out by following the procedures reported elsewhere [15,17]. The –COOH pendant group of the organic linker on the surface of NMOF**1** was activated via EDC (1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide) based on the well-known organic reaction. Then, bioconjugate with an antibody against parathion (anti-para) was formed (Fig. 1). Bioconjugation of the anti-parathion antibody was achieved through an amide linkage which led to the activation of pendant groups on the NOMF**1** surface. After the addition of parathion, the NMOF**1**/anti-parathion formed a rigid triflex structure via the hoogsteen hydrogen bonds. However, NMOF**1**/anti-parathion–parathion affinity resulted in a decrease in the observed Photoluminescence (PL) intensity. This decrease was proportional to the antigen concentration so that a linear trend was observed within a concentration range of 1 to 1000 ppb of parathion. The reduction in the PL intensity with respect to increase in the antigen concentration may be attributed to the increased wrapping of the NMOF**1**/anti-parathion probe with parathion molecules.

2.1. Materials

Cd $(NO_3)_2$, 2-aminoterephthalic acid, distilled water, anti-para (anti-parathion antibody, Methyl parathion, polyclonal, Nu-Lab, EDC (1-ethyl-3 (3-dimethylaminopropyl) carbodiimide hydrochloride), and MES (2-(N-morpholino) ethanesulfonic acid) were purchased as 99% high purity grade chemicals from Sigma-Aldrich/Merck/Fisher Scientific. The cartridges C18 (End capped) and solid phase extraction assembly were purchased from Agilent Technologies. The GC capillary column (DN-5 FAST: DANI Instruments) with a composition of 5% phenyl + 95% 95% methyl polysiloxane (0.10 mm internal diameter, 5 m column length, and 0.10 μm film thickness) was used. All other chemicals and solvents were AR/GR grade products from Sigma-Aldrich.

2.2. Equipment

Both X-ray Diffraction (XRD, Shimadzu 6000) and Field-Emission Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (FE-SEM–EDX, Hitachi 4300/SN) were used to assess the crystal phase, lattice pattern, and morphology of the prepared NMOF**1** particles. UV–visible absorption and photoluminescence spectra were also measured by UV–visible-NIR spectrophotometer (Varian Cary 5000) and PL spectrophotometer (Varian), respectively. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS10 spectrophotometer equipped with an attenuated total reflectance (ATR) accessory.

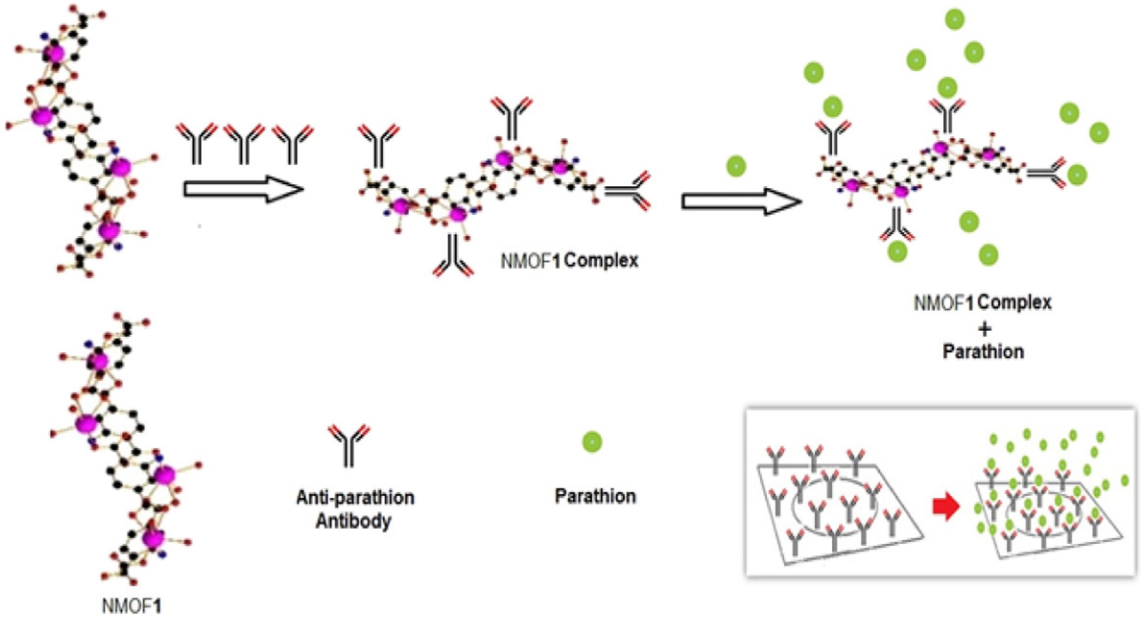

Fig. 1. Mechanism for parathion detection using NMOF**1**.