Towards metal–organic framework based field effect chemical sensors: UiO-66-NH$_2$ for nerve agent detection

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We present a highly sensitive gas detection approach for the infamous ‘nerve agent’ group of alkyl phosphonate compounds. Signal transduction is achieved by monitoring the work function shift of metal–organic framework UiO-66-NH$_2$ coated electrodes upon exposure to ppb-level concentrations of a target simulant. Using the Kelvin probe technique, we demonstrate the potential of electrically insulating MOFs for integration in field effect devices such as ChemFETs: a three orders of magnitude improvement over previous work function-based detection of nerve agent simulants. Moreover, the signal is fully reversible both in dry and humid conditions, down to low ppb concentrations. Comprehensive investigation of the interactions that lead towards this high sensitivity points towards a series of confined interactions between the analyte and the pore interior of UiO-66-NH$_2$.

Nevertheless, improved sensing materials and transducer mechanisms are still essential to elevate reliability, selectivity and response kinetics to a level suitable for commercial implementation.$^{11,12}$ Work function-based gas sensors, such as chemically sensitive field effect transistors (ChemFETs), transduce the interaction of analyte molecules with the gate electrode of a metal–insulator–semiconductor FET to a change in source-drain current. The principle underpinning signal transduction in ChemFETs is chemical modulation of the gate electrode work function through a change in surface functionalization or adsorbed surface species.$^{13,14}$ In practical devices, this work function modulation is observed as a shift in contact potential difference (CPD) relative to a reference electrode. ChemFETs are interesting for real-world applications because they are robust, highly sensitive and compatible with readily scalable, inexpensive CMOS fabrication.$^{12,15}$

Metal–organic frameworks (MOFs) are a class of crystalline porous materials that consist of metal-containing nodes connected by multtopic organic linkers.$^{16,17}$ These tailorable, high specific surface area materials show outstanding potential in catalysis,$^{18}$ gas storage$^{19}$ and molecular separations.$^{20}$ Recently, interest in integrating these materials in devices has increased rapidly,$^{21-24}$ for instance as selective adsorbent layers in various types of chemical sensors.$^{25-27}$ Although MOF-based sensors for alkyl phosphonates have not yet been developed, previous work demonstrated the suitability of MOFs as adsorptive concentrators for this family of compounds.$^{28,29}$ Recent illustrations of MOF-catalyzed decomposition of nerve gas simulants further underline the high affinity that framework building blocks such as metal oxide clusters can have for alkyl phosphonates.$^{30-32}$ The

Introduction

Detection of chemical warfare agents is both an unsolved challenge and a current need,$^4$ particularly in the context of terrorism threats. Volatile alkyl phosphonate nerve agents are a nefarious group of compounds that inhibit acetylcholinesterase (AChE), resulting in asphyxiation even at very low levels of exposure.$^2$ For example, the 10 min acute exposure guideline limit (AEGL-2) for sarin (O-isopropyl methylphosphonofluoridate, GB) is merely 15 ppb.$^3$ This compound has become infamous because of its use in the 1995 Tokyo subway attack and Gulf wars.$^4$ Dimethyl methylphosphonate (DMMP) is a widely used and relatively safe simulant (Fig. 1a). State-of-the-art metal oxide gas sensors display DMMP detection limits that are tenfold higher than required for sarin.$^5,6$ The application of designer polymer adsorbent films combined with optical and microelectromechanical transducers resulted in prototype sensors able to detect low-ppb DMMP levels under idealized conditions.$^7-10$

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$^f$Electronic supplementary information (ESI) available: Experimental section, control experiments, Kelvin probe response to humidity, water adsorption and desorption isotherms, thermogravimetric analysis, DFT calculations and Rietveld refinement data and information. See DOI: 10.1039/c6sc00987e
Herein, we report high CPD shifts of UiO-66-NH₂ covered electrodes upon exposure to DMMP concentrations down to 3 ppb in a Kelvin probe configuration. This response is generated by strong DMMP adsorption in the well-defined MOF pores, in proximity to the interface of the electrically insulating MOF and the electrode. The extrapolated (3σ) limit of detection for DMMP of the demonstrated system is 0.3 ± 0.1 ppb and the observed response time is 1.9 ± 1.3 min. This study is an important step towards implementation of MOFs in ChemFET sensors.

Results and discussion

Kelvin probe DMMP sensing using UiO-66-NH₂

The Kelvin probe technique is a well-established tool to measure the CPD between a stationary electrode and an oscillating reference electrode. The CPD consists of a bulk contribution, associated with the Fermi level of the electrodes, and a surface contribution, associated with the work function. The work function is connected to the chemical potential at the electrode surface, which is influenced by adsorption of molecules. At low analyte concentrations, this effect can be amplified by functionalizing the electrode with an adsorbent layer, to accumulate target molecules in proximity to the electrode surface. Practically, a balancing potential \( V_b = -\text{CPD} \) is determined through biasing both electrodes respectively to each other, thus zeroing the current that flows due to the oscillation of the capacitance (Fig. 1c). Kelvin probe transducers are not used as commercial sensors because of the non-scalability of the instrumentation. However, ChemFETs transduce the same analyte-induced work function shifts that are the basis of signals measured by the Kelvin probe. As the CPD change upon analyte exposure is an extensive surface property, the Kelvin probe technique is an effective macroscopic screening tool for sensing materials to be implemented in miniaturized ChemFETs (Fig. 1d).

UiO-66-NH₂ (Fig. 1b) was selected because of its superior catalytic activity in the decomposition of phosphonates. This high activity has been linked to the amino moiety that can accept protons from nearby \([\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}\) clusters and thereby induces stronger, possibly bidentate, adsorption of the phosphonates. UiO-66-NH₂ powder was drop-casted on a silicon electrode and exposed to different DMMP concentrations in a flow cell (Fig. 2a and b). Real-time Kelvin probe monitoring showed CPD shifts of tens of millivolts. These signals were reversible and consistent between repeated exposures (Fig. 2c). Moreover, the signal-to-noise ratio remained significant even at concentrations down to 3 ppb, the lowest reachable concentration for our dosing system (Fig. 2d).

The average response time \( t_{90} \) and decay time \( t_{90} \) observed for the signal over the measured concentration range was 1.9 ± 1.3 min and 5.7 ± 3.5 min respectively (Fig. S3†). The observed response time is in line with previous low concentration DMMP sensing studies using adsorptive sensing materials. The relatively slow decay of the signal indicates that desorption is rate-limiting for the signal due to high affinity of the sensing material for DMMP. Mass transport limitation through the relatively narrow pore aperture size of the MOF (ca. 0.5 nm) is another potential factor of influence.

Plotting the CPD shift signal at equilibrium in function of the DMMP concentration yields a non-linear relationship that can be fitted by an empirical Freundlich adsorption isotherm of the form \( \Delta \text{CPD} = K \sqrt{C}, \) with \( C \) the DMMP concentration in ppb and \( K \) and \( n \) fitted parameters (Fig. 2e). The extrapolated limit of detection (LOD) of this fitted relationship \( (K = 7.98 ± 1.06, n = 2.18 ± 0.22, R^2 = 0.990) \) is 0.3 ± 0.1 ppb for a 3σ noise level of 4.2 mV. To the best of our knowledge, this is the lowest LOD demonstrated to date for Kelvin probe gas sensing. Of all reported DMMP sensor types, only a capacitive ultrasonic transducer performed significantly better when used in vibration-isolated conditions (0.05 ppb LOD, 2 min \( t_{90} \)). Linear interpolation of the response in the range of the AEGL-2 level for sarin results in a sensitivity of 0.78 mV ppb⁻¹, which ...
Elucidating DMMP adsorption in the cavities of UiO-66-NH2

A ppm-range DMMP UiO-66-NH2 adsorption isotherm was measured at 300 K (saturation at 1265 ppm). This isotherm clearly reveals the high affinity of UiO-66-NH2 for DMMP, apparent from the significant uptake at low concentrations (Fig. 3a). The volumetric partition coefficient ($P_{\text{MOF/air}}$), defined as the ratio of DMMP per volume in the adsorbent and in vapor phase, is in the order of $10^6$ in the concentration region below 15 ppm. This partition coefficient is two to three orders of magnitude higher than those observed for DMMP sensing polymers, and matches the best-performing sensing material to date (DKAP, proprietary polymer, Sandia National Lab). Decreasing affinity for DMMP is observed from roughly 0.31 adsorbed DMMP molecules per zirconium atom onwards, which corresponds to 1.9 DMMP molecules per $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ cluster. This number agrees well with the number of missing linker defects estimated based on thermogravimetric analysis (Fig. S7†), and indicates that these defects are likely related with the highest-affinity DMMP adsorption sites.

Two DMMP loaded UiO-66-NH2 samples were further analyzed, at a loading of 1.2 DMMP per cluster (MOF$_{\text{DMMP-L}}$) and at a loading that is 5 times higher (MOF$_{\text{DMMP-H}}$). Together with a non-loaded UiO-66-NH2 reference sample, these samples were analyzed using gravimetric temperature programmed desorption (TPD) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). TPD reveals desorption of DMMP in the 400–450 K temperature range for MOF$_{\text{DMMP-L}}$ (Fig. 3b). Desorption occurs at slightly lower temperature than the well-described cluster dehydroxylation...
but at significantly higher temperature than a liquid DMMP reference run (full evaporation below 370 K).

This observation points toward relatively strong physisorption, which corresponds with the high affinity and fully reversible behavior observed in Kelvin probe sensing. This observation is further confirmed by ATR-FTIR (Fig. 3c). The P═O stretching mode is sensitive to nucleophilic interactions of the oxygen atom, which are accompanied by a loss of electron density of the double bond and a shift towards lower wavenumbers. This effect is clearly demonstrated by a shift between the vapor (1276 cm\(^{-1}\))\(^{44}\) and liquid phase (1230 cm\(^{-1}\)). In MOF\(_{\text{DMMP-L}}\), this P═O band is broadened and shifted to even lower (1205 cm\(^{-1}\)) wavenumbers, consistent with a strong nucleophilic interaction with the pore interior. In contrast, the measurements on MOF\(_{\text{DMMP-H}}\) show that excess DMMP, adsorbed after saturation of the strongly interacting sites, behaves similar to liquid DMMP. Desorption is observed mainly in the 350–400 K temperature range and the position of the broad P═O stretching band perfectly matches the liquid phase value. Importantly, only a small shift is observed for the C═O stretching modes of the methoxy substituents (1022 to 1034 and 1053 to 1056 cm\(^{-1}\)) in all cases, indicating no dissociative adsorption or hydrolysis of DMMP.

To obtain further insight in the adsorption of the DMMP molecule in UiO-66-NH\(_2\), periodic static and dynamic density functional theory (DFT) calculations were carried out. The calculations were performed on a UiO-66-NH\(_2\) structure containing clusters with isolated missing linker defects (Fig. S8\(^{†}\)).\(^{52,53}\) These simulations reveal two plausible adsorption sites, as shown in Fig. 3d. Firstly, adsorption may occur in a position adjacent to a missing linker in the octahedral cage. In this adsorption site long range interactions occur between the amino groups and the DMMP molecule. Secondly, the DMMP molecule may adsorb directly in the position of a missing linker, where it interacts closely with the water molecules and hydroxides capping the defect sites on the cluster. Both sites show a roughly equal electronic adsorption energy of 100 kJ mol\(^{-1}\).§ To give a view on the mobility of the adsorbate in...
the framework, we performed 20 ps molecular dynamics runs at 300 K starting from both adsorption positions. The adsorbate configuration of the DMMP molecules as obtained from static calculations was maintained during the whole simulation, which further underlines the strong adsorption of DMMP on both sites.

High-resolution powder X-ray diffraction patterns of MOF$\text{DMMP}$ were recorded to localize electron density associated with adsorbed DMMP in the pores of UIO-66-NH$_2$. Rietveld refinement of a framework containing a rigid PO$_4$ tetrahedron as guest model was performed to approximate the position of the central phosphorus atom of the DMMP molecule (Fig. S11 and Table S1, Dataset S1$^\dagger$). Following convergence ($R_{wp} = 3.3\%$), this model fragment is situated on a position (Wyckoff multiplicity 192) in the framework’s octahedral cavity (Fig. 3e). In a fully connected UIO-66-NH$_2$ lattice, this PO$_4$ position would overlap with the framework atoms, which supports a correlation between the missing linker defects and the highest affinity adsorption sites. The refined position of the phosphorus site in the octahedral cage complies reasonably well with one of the two adsorption sites obtained by DFT modelling (Fig. S12$^\ddagger$). Due to the disordered nature of the missing linkers, it is not possible to conclusively refute the occurrence of the second adsorption site based on X-ray diffraction.

Conclusions

We demonstrated the potential of UIO-66 type MOFs in work function-based sensors for alkyl phosphate nerve agents. Through Kelvin probe monitoring, the nerve agent simulant DMMP was reversibly detected, both in dry and humid conditions, down to low ppb concentrations. The high sensitivity of UIO-66-NH$_2$ results from a series of confined interactions of DMMP in the octahedral lattice pocket in proximity to missing linker defects. Our study indicates that integration of MOF sensing materials is an interesting pathway for tailoring of ChemFETs to obtain unmatched sensing performances. In addition, our results show that the electrically insulating nature of typical MOFs does not inevitably lead to a limited suitability for field effect and other potentiometric chemical sensors. The available toolbox of MOF design strategies offers a broad perspective for detection of analytes based on different interactions. Moreover, recent progress in computational screening of MOFs for specific adsorption properties and applications can considerably facilitate optimal matching of analytes and sensing materials.$^{34,55}$

Author contributions

I. S., R. A., P. M. V. and R. V. S. developed the concept. I. S. conducted material synthesis and characterization, analyzed the data and drafted the manuscript with guidance from R. A. and D. D. V. B. B., H. R. and N. S. carried out the structure refinement. J. F. M. O. and D. W. performed the KP experiments. J. H. and V. V. S. conducted the DFT calculations. All authors discussed the results, contributed to writing the manuscript and commented on it.

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Notes and references

† Control experiments showed no signal due to DMMP interaction with the substrate (Fig. S1). Preliminary MOF screening experiments showed a higher signal for UIO-66-NH$_2$ in comparison to a set of other candidates (Fig. S2).
‡ The individual enthalpic and entropic contributions and atomic charges for both adsorption sites are given in Tables S1–S3, Fig. S9 and S10.