

Cite this: *RSC Adv.*, 2019, 9, 7615

Qualitative colorimetric analysis of a Ir(III)/Eu(III) dyad in the presence of chemical warfare agents and simulants on a paper matrix†

 Genevieve H. Dennison,^a Christophe Curty,^b Alexander J. Metherell,^c Eva Micich,^a Andreas Zaugg^b and Michael D. Ward^d
Received 31st January 2019
Accepted 26th February 2019

DOI: 10.1039/c9ra00824a

rsc.li/rsc-advances

The addition of G- and V-series organophosphorus chemical warfare agents and simulants to a paper-based assay of a dual-luminescent Ir(III)/Eu(III) dyad generated different emissive responses between the classes and compound types. The emission responses are complex and based not only on altering the balance between red Eu(III)-based and blue Ir(III)-based luminescent components, but also incorporate other factors such as analyte volatility, concentration and UV absorption. The extent of this emission colour change was analysed colorimetrically and related to the change in RGB output over time.

The traditional organophosphorus chemical warfare agents (OP CWAs) comprise two main series of agents: the G- and V-series (examples GB and VX respectively, Fig. 1). Although the G- and V-series OP CWAs display differing structural and physico-chemical properties (*e.g.* volatility), these chemicals are all fast-acting and potent acetylcholinesterase inhibitors that can cause incapacitation or death rapidly upon exposure.¹ Thus, fast and reliable chemical sensing methods are required to inform and protect military and national security first responders and the general public.

Trivalent lanthanide [Ln(III)] complexes that display characteristic strong luminescence in the visible region are being increasingly exploited for the luminescence-based sensing of OP CWAs due to their known ability to form coordinative bonds with phosphonyl and phosphoryl moieties.² In addition, the trivalent lanthanide complexes display high intensity and narrow emission bands, long excited state lifetimes and substantial Stokes shifts which provide attractive foundations for luminescence-based sensing systems.³

Previously we reported the solution-state emissive behaviour of an Ir(III)/Eu(III) dyad (denoted **Ir·L·Eu**, Fig. 2) as the basis of a ratiometric sensor for the V-series simulant 2-diisopropylaminoethyl ethyl methylphosphonate (VO).⁴ Upon excitation of this **Ir·L·Eu** dyad, photoinduced energy transfer from the ³MLCT/³LC excited-state of the Ir(III) complex to the lower-lying ⁵D₀ excited state of the Eu(III) ion results in the sensitised red luminescence from the Eu(III) centre with concomitant partial quenching of the Ir(III) blue emission.⁵ Titration of VO aliquots into a solution of **Ir·L·Eu** resulted in a sequential colour change of the emission from red through to blue (ESI Fig. S1(a)†).⁴ This emission colour 'switch' is the result of both static and dynamic luminescence quenching of the Eu(III) complex arising from the presence of VO. In particular, bidentate chelating coordination of VO to the Eu(III) ion displaces the {Eu(hfac)₃} unit from the **Ir·L·Eu** dyad (Fig. 2). This resulted in the loss of sensitised Eu(III)-based emission and restoration of the blue Ir(III)-based emission.^{4,6} Additional quenching of any residual Eu(III)-based emission occurs by photoinduced electron transfer from the tertiary amine unit of either chelated VO, or by collision with excess VO in solution (Scheme 1).^{4,6}

There are numerous other literature examples of lanthanide-based sensors for the detection of OP CWAs, simulants, pesticides and toxic industrial chemicals.^{2,6–14} Whilst many of these

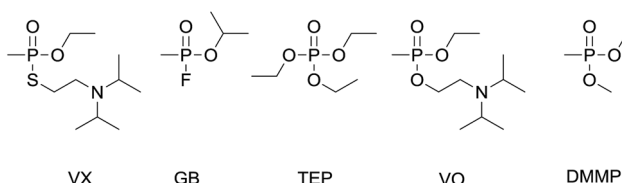


Fig. 1 The chemical structures of the G and V-series chemical warfare agents VX (2-diisopropylaminoethyl ethyl methylphosphonothiolate) and GB (Sarin, isopropyl methylphosphonofluoridate) and simulants TEP (triethyl phosphate), VO (2-diisopropylaminoethyl ethyl methylphosphonate) and DMMP (dimethyl methylphosphonate) utilised in this investigation.

^aLand Division, Defence Science and Technology Group, Fishermans Bend, Melbourne, Australia. E-mail: Genevieve.Dennison@dst.defence.gov.au

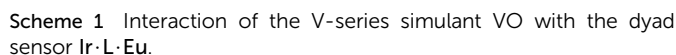
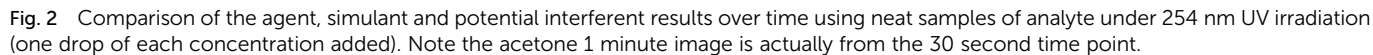
^bOrganic Chemistry Branch, Federal Office for Civil Protection (FOCP), Spiez Laboratory, Spiez, Switzerland

^cDepartment of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

^dDepartment of Chemistry, University of Warwick, Coventry, CV4 7AL, UK. E-mail: m.d.ward@warwick.ac.uk

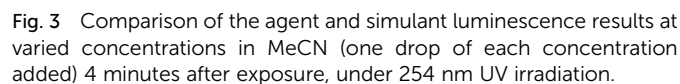
† Electronic supplementary information (ESI) available: Full experimental methods, photographs, RGB data and analysis. See DOI: 10.1039/c9ra00824a





The **Ir·L·Eu** dyad paper assays were prepared on Whatman 1 filter paper as described in the ESI.[†] One drop of a neat analyte was then placed on a test strip and images of the emissive

Two modes of visual comparison were performed to generate qualitative results: (i) a general comparison of all neat CWAs, simulants and interferents at varied time points to understand which systems would result in a visual change (Fig. 2); and (ii) a targeted comparison of the agent and simulant data at varied concentrations at a time point more suitable for in field testing (Fig. 3). The visual comparison of agent and simulant response over time using neat compounds (Fig. 2) generated some unexpected results in comparison to the solution studies with VO.⁴ VX and its simulant VO gave a very dark blue-black response that correlated well with each other over all time points. GB, however, displayed minimal colorimetric changes up to 5 minutes with the bright blue Ir(III) luminescence seen only at the 1 hour time point (Fig. 2). This increased time of detection was initially attributed to a reactive pathway that can occur with the G-series CWAs only (hydrolysis of the P-F bond and subsequent detection of F⁻).^{2,8} However, when the similar (neat) results of the non-reactive G-series simulant DMMP (which does not contain a P-F bond) are considered this pathway is called into question. Whilst some competitive binding (Scheme 1) likely occurs with VX, VO, GB and DMMP at early time points, the excess analyte also absorbs the UV-light.¹⁵



Presumptive tests taking 1 hour are well outside of operational requirements in the field. However, the time to detection could be lowered in this assay by decreasing the concentration of the analyte or *via* the application of heat or airflow to facilitate evaporation of excess analyte. The use of such processes to accelerate the development of the results is not unprecedented in analytical chemistry (*e.g.* TLC plate development) and with

Whilst many of the analytes gave emission changes that can be observed with the naked eye (under UV light illumination); many of the responses are variations of the blue emission which may be too subtle to allow visual differentiation between OP compounds and other analytes. Thus interpretation of the results of these systems can be subjective and/or rely upon visual acuity in high stress situations. To combat this we analysed the photographic results to generate RGB colorimetric data for potential application into colour reading technologies to facilitate the reliable, fast and accurate interpretation of results in the field and to differentiate between the outputs obtained with various analytes. The images were processed as outlined in the ESI† and loaded into the colorimetric program Spot Finder 1.13 (iSense).¹⁸ An area in the centre of the spot formed upon liquid application with the most even colouration was selected for analysis and the averaged RGB data generated. The percentage change in intensity over time (300 seconds) for each RGB colour element at each concentration point was plotted to give a visual representation of the colorimetric changes occurring over the experiment. Fig. 4 demonstrates the RGB plots of the luminescence responses for the application of neat VX, VO, GB and DMMP over 5 minutes (300 seconds). From this analysis it can be seen that VX and VO generate greater colorimetric differences in the blue component compared to GB and DMMP. VX results in near complete loss of the red and



Fig. 4 Colorimetric time response profiles (smoothed data) over 300 seconds by percentage change in each of the R, G and B colour components for neat and 0.05 M VX, VO, GB and DMMP.

green components of the dyad and majority (~85% loss) of the blue component with no recovery of any colour component over the experiment time; whilst VO only demonstrates complete loss of the red component with significant recovery of the blue component after approximately 60 seconds. It should be noted that increases in the blue component are observable in VX and VO down to 0.01 M (ESI Fig. S4 and S8†). When looking at the G-series results, GB displays partial loss of the red component with a substantial increase in the blue component which is a trend observable down to 0.05 M (Fig. 4). DMMP however, displayed less significant increases in the blue component observed with GB at neat concentrations but demonstrated more when diluted (ESI Fig. S10†). This is again most likely due to the reduced amounts of excess analyte present at the lower concentrations.

Conclusions

The luminescent dyad **Ir·L·Eu** paper assay, which contains both red and blue luminescent components, displays different luminescent responses in the presence of a variety of OP CWAs, simulants and interferents. The colorimetric (emission) responses are complex and based not only on altering the balance between red and blue luminescent components by a range of quenching mechanisms, but also incorporate other factors such as analyte volatility (wetting), concentration and UV absorption.

We have demonstrated that the Ir(III)/Eu(III) dyad paper assay for the presumptive detection of chemical warfare agents can be utilised, under UV-light excitation, to provide a clear visual response to differentiate between different CWA classes (G and V) as well as demonstrating some differentiation between the core functional groups of various phosphorus systems

(phosphate, phosphite, phosphonate). The fast recovery of the red luminescence when exposed to many common interferents is promising as is the paper assay's resistance to significant interference from water.

Although signal development did take significant time for some neat analytes, we demonstrated that appearance of the GB signal could be hastened by dilution. It is also feasible that heat or airflow could be introduced to facilitate signal development in the future. RGB colorimetric analysis can be applied to differentiate between similar compounds (*i.e.* VX and VO) suggesting that the use of handheld colorimetric readers (with inbuilt UV light sources) may be a feasible way to overcome issues of visual acuity by providing more colorimetric information to reduce the likelihood of false positives from similar compounds. This luminescent dyad system could also be applied to fluorescent/colorimetric arrays that distinguish between many types of OP CWAs, simulants and interferents.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

G. H. D. extends her thanks to the Chemical and Biological Defence Branch (Land Division, DST Group) for funding and support to this work and to Assoc. Prof. Kellie Tuck (Monash University) and Drs David Nielsen and Gregory Barbante (DST Group) for their assistance in proof reading this manuscript. The provision of financial support does not constitute an express or implied endorsement of the results or conclusions presented here by DST Group or the Australian Department of Defence.



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