


## 1 Fluorescent Discrimination between Traces of Chemical Warfare Agents and Their Mimics

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9  Supporting Information

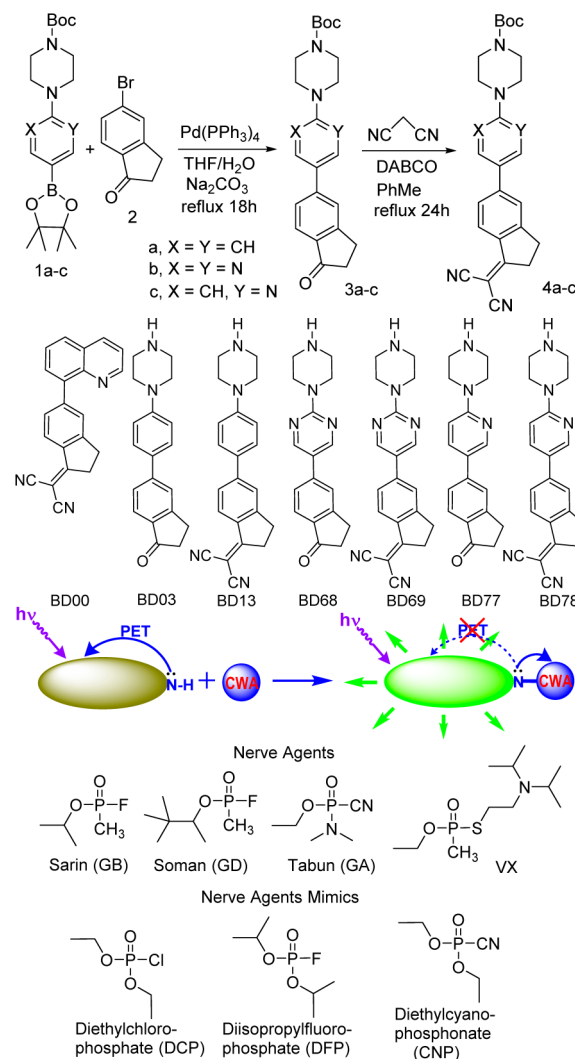
10 **ABSTRACT:** An array of fluorogenic probes is able to  
 11 discriminate between nerve agents, sarin, soman, tabun,  
 12 VX and their mimics, in water or organic solvent, by  
 13 qualitative fluorescence patterns and quantitative multi-  
 14 variate analysis, thus making the system suitable for the in-  
 15 the-field detection of traces of chemical warfare agents as  
 16 well as to differentiate between the real nerve agents and  
 17 other related compounds.

18 Nerve agents are highly toxic volatile liquids that  
 19 irreversibly block the enzyme acetylcholinesterase in the  
 20 neuronal synapsis, thus disrupting nerve impulse transmission  
 21 and causing death through the paralysis of respiratory muscles.<sup>1</sup>  
 22 They are used as chemical warfare agents (CWA) for dirty war  
 23 in undeveloped countries, causing hundreds of victims,  
 24 although their use as chemical weapons is prohibited.<sup>2</sup> Their  
 25 quick detection can be achieved by hand-held instruments that  
 26 are costly and prone to false positives<sup>3</sup> so the availability of safe  
 27 and easy to use portable devices is most sought-after. More  
 28 importantly, the investigation of chemical weapons allegations  
 29 is a very slow process that implies unequivocal detection of  
 30 CWA residuals in water and organic samples,<sup>4</sup> with the risk of  
 31 long delays in the environment of worrying war scenarios.<sup>5</sup>  
 32 Colorimetric<sup>6</sup> or fluorimetric<sup>7</sup> reactive dyes in solution or as  
 33 arrays,<sup>8</sup> as well as supported in nanomaterials,<sup>9</sup> have been used  
 34 for fast detection of CWA as good alternatives to classic  
 35 methods, but most of these methods are implemented for nerve  
 36 agents mimics, and so there is no clear proof that they will work  
 37 for real CWA.<sup>10</sup> To complement the existing methodologies,  
 38 we have developed a series of new highly solvatochromic  
 39 fluorescent indicators for phosphorylating reagents capable of  
 40 developing large differences in fluorescence. In this paper, we  
 41 report our findings upon the selective fluorescent discrimi-  
 42 nation of real nerve agents from their mimics.

43 We have previously prepared some charge-transfer fluoro-  
 44 genic probes, bearing conjugated donor and acceptor groups in  
 45 their structure, that were useful for the detection of significant  
 46 analytes.<sup>11</sup> For our current purpose we have designed new  
 47 fluorescent probes (Scheme 1).

48 In this case, they have a secondary donor group that was not  
 49 involved in the charge-transfer process. Thus, the Suzuki

Scheme 1. Synthesis of Fluorescent Probes and Their Action



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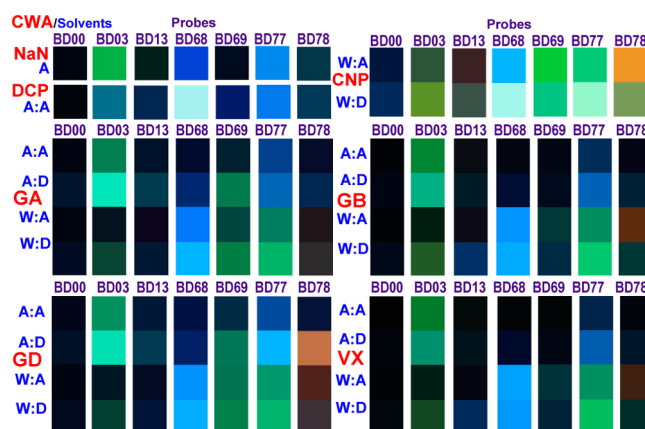
50 reaction of aryl boronates **1a–c** and 5-bromoindanone **2**  
 51 catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> in tetrahydrofuran/water in the  
 52 presence of Na<sub>2</sub>CO<sub>3</sub> gave arylindanones **3a–c** in 85–95%  
 53 yields. Knoevenagel reaction of **3a–c** and malononitrile in the  
 54 presence of DABCO in toluene at reflux for 24 h gave  
 55 arylindanes **4a–c** in 55–68% yields. *N*-Boc deprotection with  
 56 trifluoroacetic acid for 15 min from **3a–c** and **4a–c** gave the  
 57 unprotected amine derivatives BD03, BD13, BD68, BD69,  
 58 BD77 and BD78, in which the initial fluorescence of **3a–c** and  
 59 **4a–c** is quenched in some extension by a photoinduced  
 60 electron transfer from the free amine group. Subsequent  
 61 acylation or phosphorylation of the amine group should  
 62 therefore increase fluorescence of these compounds, thus  
 63 making these compounds suitable for phosphorylating agents  
 64 detection (Scheme 1). Fluorescence of these compounds can  
 65 be also affected by protic acids, therefore we added to the series  
 66 a fluorogenic dye, BD00,<sup>12</sup> which is not fluorescent but  
 67 develops a blue fluorescence in the presence of common protic  
 68 acids. In this way, false positives are prevented. We next tested  
 69 10<sup>-4</sup> M solutions of the seven fluorescent probes in  
 70 dimethylsulfoxide (DMSO) or acetonitrile (MeCN) with 1  
 71 equiv of 5 × 10<sup>-3</sup> M solutions of nerve agent simulants (DCP,  
 72 DFP, CNP) (Scheme 1) and phosgene<sup>13</sup> (Cl<sub>2</sub>CO) in MeCN or  
 73 water and recorded all changes that the fluorescent probes  
 74 underwent with every analyte under a common TLC-UV light,  
 75 λ = 366 nm, by qualitative (photographs) and quantitative  
 76 measurements such as initial and final λ<sub>max</sub><sup>abs</sup> and λ<sub>max</sub><sup>fluo</sup>,  
 77 variations in the relative intensity of fluorescence and kinetics of  
 78 processes. The qualitative measurements gave clear and distinct  
 79 fingerprints of every nerve agent mimic used for testing the  
 80 probes, undoubtedly discriminating between them. The  
 81 quantitative measurements were subjected to hierarchical  
 82 cluster analysis (HCA).<sup>8</sup> HCA dendrogram obtained from  
 83 fluorescent measures showed a clear clustering for all the nerve  
 84 agent simulants, blank and phosgene, giving a good separation  
 85 of every analyte (Figure S65b). Absorbance or mixed data from  
 86 absorbance and fluorescence afforded a poor separation  
 87 between some analytes (Figures S64 and S65a), therefore  
 88 establishing that discrimination between analytes is best  
 89 obtained by fluorescence measurements. Likewise, principal  
 90 components analysis (PCA)<sup>14</sup> of the same data afforded good  
 91 discrimination between each one of the CWA mimics as well as  
 92 phosgene (Figure S66), therefore probing that the array of  
 93 fluorescent dyes is able to discriminate between closely related  
 94 phosphorylating or acylating reagents by both their fingerprints,  
 95 HCA or PCA. The next step was testing the system with real  
 96 nerve agents, but because of the extreme toxicity we performed  
 97 the tests at the laboratories of the FOI CBRN Defense and  
 98 Security (Umeå, Sweden), where handling of nerve agents was  
 99 performed under appropriate conditions. Again, the seven  
 100 different fluorescent probes were mixed with a series of nerve  
 101 agents, Soman, Sarin, Tabun, and VX and chemically similar  
 102 substances diethylchlorophosphate (DCP) and diethylcyano-  
 103 phosphonate (CNP), in the same conditions used for CWA  
 104 mimics. The acquired samples of mixtures were then subjected  
 105 to light (300–500 nm) in which they fluoresced with different  
 106 colors. Light intensities were registered with a spectrofluor-  
 107 ometer and photographs were taken for a chart of visible colors  
 108 of all the test samples. The probes and CWA were solved in  
 109 two different solvents, DMSO and MeCN for the probes, and  
 110 MeCN and water for the CWA/CWA-simulants. The probes  
 111 were also tested without CWA or simulant. The acquired  
 112 mixtures were named as in the following example: Sarin solved

in water mixed with probe DM13 solved in DMSO was called  
 GB\_W13D. For the mixtures with only probes the name begins  
 with NaN. To photograph the samples they were placed under  
 a 366 nm UV-lamp in a dark room. A color reference sheet  
 illuminated with white light was placed nearby (Figure S89).  
 Copies of the RAW-files were edited, all in the same way (batch  
 process), before being converted to JPG for extraction of the  
 colors as RGB-values. Both the colors from the edited images  
 and from the original images were analyzed. As an example, a  
 photograph of Soman samples is seen in Figure 1.



**Figure 1.** Samples contained Soman in MeCN mixed with each of the seven probes in DMSO. From left to right the samples contained probes BD00 to BD78.

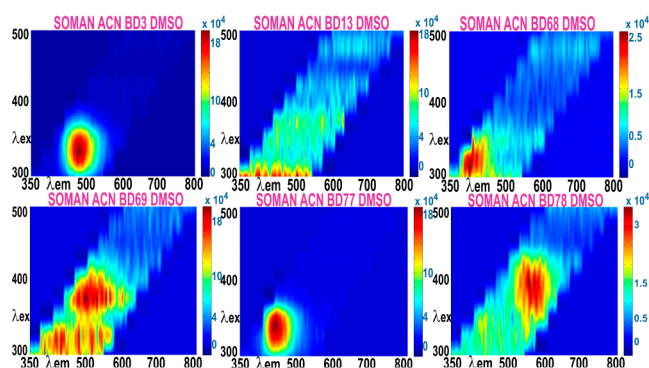
Since there were three images of every set of seven samples, the mean values in R, G, and B had to be computed. A table of these colors in the form of colored squares was then created as seen in Figure 2. Looking at the tables of observed colors it was



**Figure 2.** Observable colors in 366 nm excitation light. CWA: Sarin (GB), Soman (GD), Tabun (GA), VX (VX). CWA-simulants: CNP and DCP. CWA/simulants solvent: water (W) and acetonitrile (A). Probes: BD00, BD03, BD13, BD68, BD69, BD77, BD78. Probe solvents: dimethylsulfoxide (D) and acetonitrile (A).

clear that several probes could be used to guarantee the absence  
 of Sarin, Soman, Tabun, and VX. For some choices of solvents  
 there was a possibility to make the distinction between Soman  
 and the other CWA. If a sample with probe BD69 in  
 acetonitrile fluoresced very weakly (as in probe BD69 in  
 acetonitrile, known as NaN A in the table of observed colors),  
 then the risk of there being Sarin, Soman, Tabun, or VX in the  
 samples is low since the corresponding CWA samples, with  
 nerve agent in water and probe in acetonitrile, all fluoresced  
 green. Probe BD78 acts in a similar way, but here the CWA-  
 samples fluoresced in orange, while for probe BD03 it is the  
 other way around. The NaN A sample with probe BD03  
 fluoresced in bright green, while there is barely any fluorescence  
 from the corresponding CWA samples. Probe BD77 also gave  
 valuable information but in a different way. For this probe both  
 the probe and the CWA samples fluoresced clearly, but the

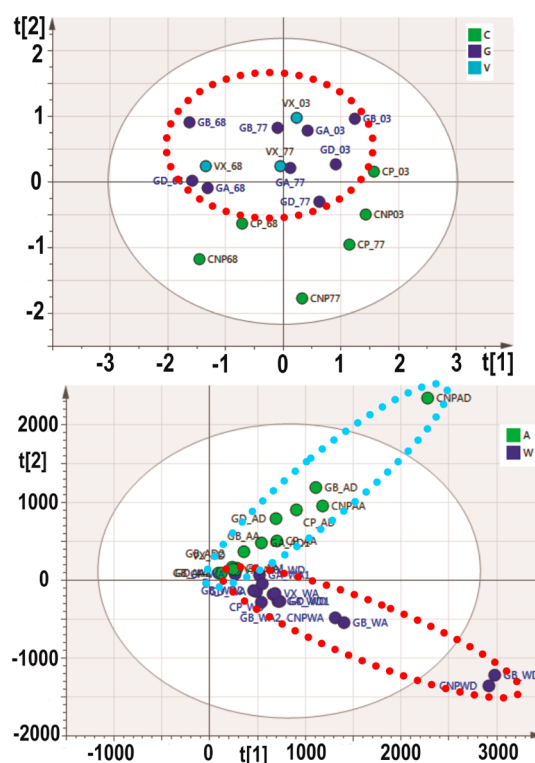
143 probe samples did so in blue, while the CWA samples all  
 144 fluoresced in green. It was probe BD78 that indicated that there  
 145 was a possibility to distinguish Soman from the rest of the  
 146 CWA. It is visible in the Figure 2 of observed colors that the  
 147 mixture of Soman in MeCN and probe in DMSO fluoresced in  
 148 a clear orange color, while the rest of the CWA samples with  
 149 the same solvents fluoresced with weak obscure blue color. A  
 150 table with the colors from the unedited images can also be  
 151 found in Figure S90. The colors from preliminary experiments  
 152 with only simulants have been included in a similar table in  
 153 Figure S92. For quantitative measurements we used a calibrated  
 154 spectrofluorometer. In the analysis of the spectral data a  
 155 multivariate data analysis with Simca<sup>15</sup> software was used. To  
 156 analyze the data we used a couple of approaches. Some of the  
 157 basic analysis was made just by looking at the plots of the  
 158 spectroscopy data. We were able to see that some of the  
 159 mixtures just gave fluctuations in the data, while other gave  
 160 clear tops. We found that the probes BD03, BD68, and BD77  
 161 were the probes that gave the highest number of clear tops,  
 162 while the other only gave a few clear tops. In Figure 3 six



**Figure 3.** Plots of the spectrofluorometer data for CWA Soman (GD) solved in MeCN with the probes BD03 to BD78 in DMSO. In the plots we see how probe BD13 (top middle) causes fluctuations over the whole spectra while the probes BD03 and BD77 (top left and bottom middle) have very clear spectra. One of the few tops of probe BD78 (bottom right) can be seen and it is also this clear orange color that makes Soman stand out from the other CWA in the photographs.

163 spectra for Soman are plotted, showing all types of spectra that  
 164 occurred, along with the distinct spectra for probe BD78 that  
 165 distinguished Soman from the other probes in the spectra as  
 166 well as in the photographs.

167 By use of multivariate data analysis we found that we were  
 168 able to detect in which solvent the CWA were solved. We were  
 169 also able to see a clear difference between the probes that gave  
 170 clear tops in the spectrofluorometer data, and those that did  
 171 not. In the analysis of the spectrofluorometer data the measured  
 172 values were emission ( $\lambda_{em}$ ) and excitation ( $\lambda_{ex}$ ) wavelengths,  
 173 and intensity of the maximum (fl\_max) in each of the produced  
 174 two-dimensional spectra. We also calculated the area in the  
 175 spectra with intensities of 50% and 75% or more of the  
 176 maximum (area50 and area75, respectively). We were able to  
 177 see a clear difference between the simulants and the CWA  
 178 when performing a multivariate analysis on agent-probe  
 179 combinations (Figure 4). After our analysis we can conclude  
 180 that there is a large probability that the probes are able to detect  
 181 the most important CWA from their mimics. In the analysis  
 182 only probes BD03, BD68, and BD77 were used to avoid the  
 183 fluctuations, as variables we used area50,  $\lambda_{ex}$ ,  $\lambda_{em}$ , and fl\_max for



**Figure 4.** (Upper) A plot of the first two principal axes when running a multivariate analysis over the agent-probe combinations. In the plot we see a clear separation of the CWA (G and V) and the simulants (C). In this plot only the probes BD03, BD68, and BD77 were used, i.e., the probes that did not have a large tendency to fluctuate. (Down) A plot of the first two principal axes when running a multivariate analysis over the agent-solvent combinations. In the plot we can see a clear separation of the agents solved in water and those solved in acetonitrile.

each of the four solvent combinations. Before the PCA analysis  
 was run all data were transformed logarithmically and grouped  
 in blocks of  $\lambda_{em}/\lambda_{ex}$ , fl\_max, and area50 before unit variance  
 was run. From the load vectors for the analysis of the agent-  
 probe combinations (Figure S72) we could see how the areas  
 and fluorescence were the main parameters for the second  
 component. In addition, the simulants generally had a bit  
 higher fluorescence and for some a bit smaller areas, therefore  
 they tended toward the lower values on the second component.  
 When studying the combinations of agent and solvents against  
 probes we were able to see a clear separation between the  
 agents that were solved in water and those that were solved in  
 acetonitrile. This can clearly be seen in Figure 4, the main  
 reason behind this separation seems to be that the intensity of  
 probe BD68 becomes higher for those agents solved in water  
 (Figure S88).

In summary, we have synthesized a new series of fluorogenic  
 probes that are able to discriminate between traces of CWA and  
 their mimics, in water or organic solvent. Discrimination is  
 achieved by means of the different fluorogenic response  
 triggered by CWA or their mimics on the fluorogenic probes  
 in different solvent combinations of CWA and probes.

The different response given by the series of fluorogenic  
 probes is charted as a fingerprint of the fluorescent response of  
 every CWA/probe/solvent combination under a common 366  
 nm UV light, thus permitting a fast visual differentiation  
 between CWA and their mimics. More accurate discrimination

211 is achieved by multivariate analysis by using quantitative  
212 measurements in fluorescence spectroscopy. In this way we  
213 have obtained a complete differentiation between CWA and  
214 their mimics, so the system is suitable for the accurate in-the-  
215 field detection of traces of CWA. We have seen that the  
216 response given by CWA mimics is very different to the  
217 response given by the real CWA, because of the slightly  
218 different chemical functionality of CWA and their mimics.  
219 Since most of the chromogenic and fluorogenic probes hitherto  
220 studied for the detection of CWA are based in the study of the  
221 response given by their mimics, there is no guarantee that  
222 previously known probes for CWA mimics will work with real  
223 CWA samples. Our work clearly shows that the response can be  
224 very different. In addition, the synthesis of the reported  
225 fluorogenic probes is simple and straightforward, therefore  
226 these fluorescent probes are suitable for the development of  
227 upcoming practical methodology.

## 228 ■ ASSOCIATED CONTENT

### 229 ● Supporting Information

230 Experimental details and characterization data. This material is  
231 available free of charge via the Internet at <http://pubs.acs.org>.

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### 236 Notes

237 The authors declare no competing financial interest.

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