SUPPORTING INFORMATION

Supramolecular Detection of Sub-ppm Nerve Agents Simulant by Smartphone Tool

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2.1 General experimental methods.

The NMR experiments were carried out at 27° C on a Varian UNITY Inova 500 MHz spectrometer (^{1}H at 499.88 MHz, ^{13}C NMR at 125.7 MHz) equipped with pulse field gradient module (Z axis) and a tuneable 5 mm Varian inverse detection probe (ID-PFG). ESI mass spectra were acquired on an API 2000– ABSciex using CH_3CN or CH_3OH (positive or negative ion mode). A JASCO V-560 UV-Vis spectrophotometer equipped with a 1 cm path-length cell was used for the UV-Vis measurements (resolution 0.1 nm). Luminescence measurements were carried out using a Cary Eclipse Fluorescence spectrophotometer with resolution of 0.5 nm, at room temperature. The emission was recorded at 90° with respect to the exciting line beam using 5:5 slit-widths for all measurements. All chemicals were reagent grade and were used without further purification.

2.2 Procedure for fluorescence titration

Two mother solutions of receptor and DMMP (1.0×10^{-3} M) in $CHCl_3$ were prepared. From these, different solutions with different receptor/guest ratios were prepared (in cuvette, probe concentration was fixed at 1×10^{-6} M, while increased amounts of DMMP were added), and emission spectra were recorded at 25 °C. The apparent binding affinity values were estimated using HypSpec (version 1.1.33) [17], a software designed to extract equilibrium constants from potentiometric and/or spectrophotometric titration data. HypSpec starts with an assumed complex formation scheme and uses a least-squares approach to derive the spectra of the complexes and the stability constants. χ^2 test (chi-square) was applied, where the residuals follow a normal distribution (for a distribution approximately normal, the χ^2 test value is around 12 or less). In all of the cases, $\chi^2 \leq 10$ were found, as obtained by 3 independent measurements sets. Limit of detection was calculated trough the method of the calibration curve using the formula LOD = $3\boldsymbol{\sigma}$/K, where s is the standard deviation of the blank, and K is the slope of the calibration curve. Fluorescence quantum yields (Φ_F) were estimated by using *N*-butyl-4-butylamino-1,8-naphthalimide as a standard, $\Phi_F = 0.81$.

2.3 Determination of Stoichiometry.

Stoichiometry of the complex was investigated by the Job's plot method, using spectrophotometric measurements. The samples were prepared by mixing equimolecular stock solutions (1.0×10^{-3} M) of the receptor and DMMP to cover the whole range of molar fractions, keeping constant the total concentration (1×10^{-6} M). The changes in absorbance compared to non-complexed receptor species ($\Delta A \times \chi^{-1}$) were calculated and reported versus the receptor mole fraction (χ). These plots show a maximum at 0.5 mol fraction of receptor, thus suggesting its 1:1 complex formation.

2.4 Procedure for sensing by Test Strip.

One microliter of a solution of **BDPy-NH$_2$-AE** (1×10^{-3} M in CH_2Cl_2) was adsorbed onto a RP-18 silica gel foil (1 × 2.5 cm) and solvent was removed under air flow at room temperature. These foils

were inserted into a vial (23 mL) containing a precise amount of DMMP (solution of DMMP in CH_2Cl_2 at different concentrations, exposed to the supported sensor for 1 h at 50°C), to reach the concentration values reported in the main text. These vials were maintained at 50°C for 1 h. After this time, samples were observed under UV−vis lamp at 365 nm (UV-Vis lamp power 6W) in a dark chamber. The position of the samples into the dark chamber is maintained at 20 cm from the smartphone and UV source. The images have been elaborated by Fiji. In particular, images have been converted in RGB channel values, and converted into Gray scale value (G) by using the formula G=(Rvalue + Gvalue +Bvalue)/3, thus obtaining a single value for each pixel. The emission intensities of this scale for each concentration value have been compared to the control (carbon nanoparticles), and these normalized values (ratio between the intensity of the **BDPy-NH_2-AE** probe and the intensity of the control) have been reported. The resulting values were tabulated for statistical treatment using the Excel software (Microsoft 365).

2.5 Procedure for Recovery.

Recovery tests were performed by thermal treatments. In particular, in a closed 23 mL vial were introduced the solid support, containing the receptor and the control, and 1 mL of DMMP. Vial was heated at 50 °C for 1 h, then the image has been acquired and elaborated as previously described. Then the solid support has been heated at 50 °C for 1 h into a ventilated oven, and the image has been acquired. This thermal treatment leads to the recovery of the starting sensor. Then, another DMMP exposure has been repeated.

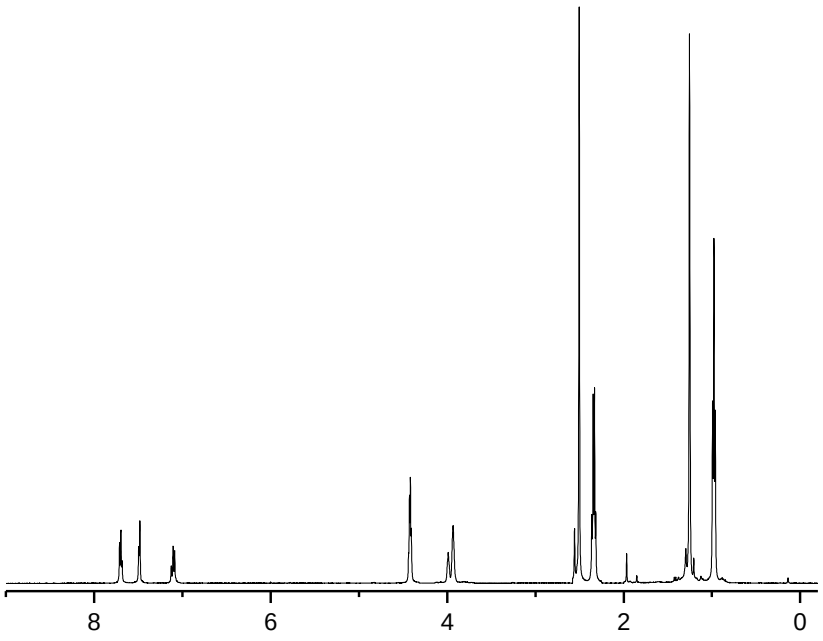


Figure S1: ^{1}H NMR spectrum of **BDPy-NH$_2$-AE** in acetone-d_6

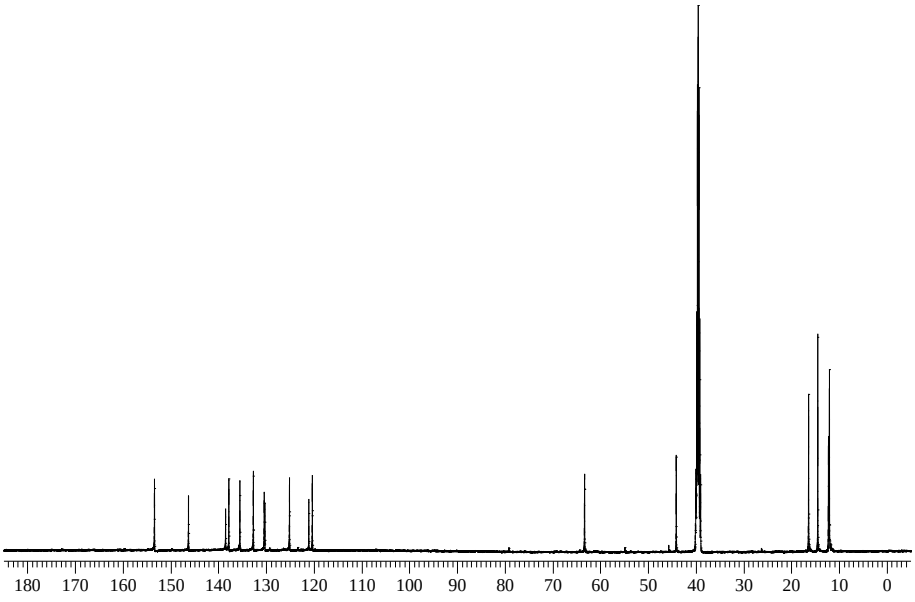


Figure S2: ^{13}C NMR spectrum of **BDPy-NH$_2$-AE** in DMSO-d_6

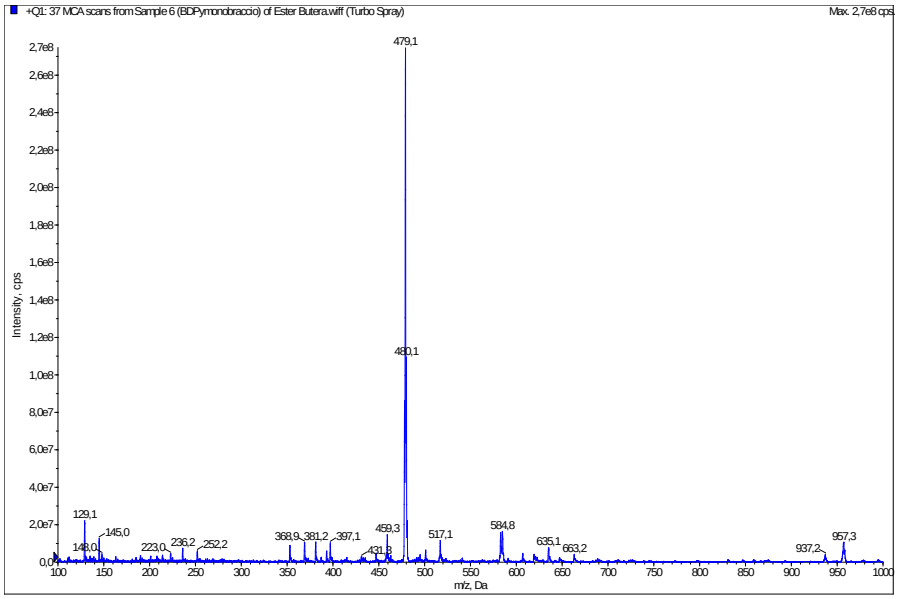


Figure S3: ESI-MS spectrum of **BDPy-NH_2-AE**

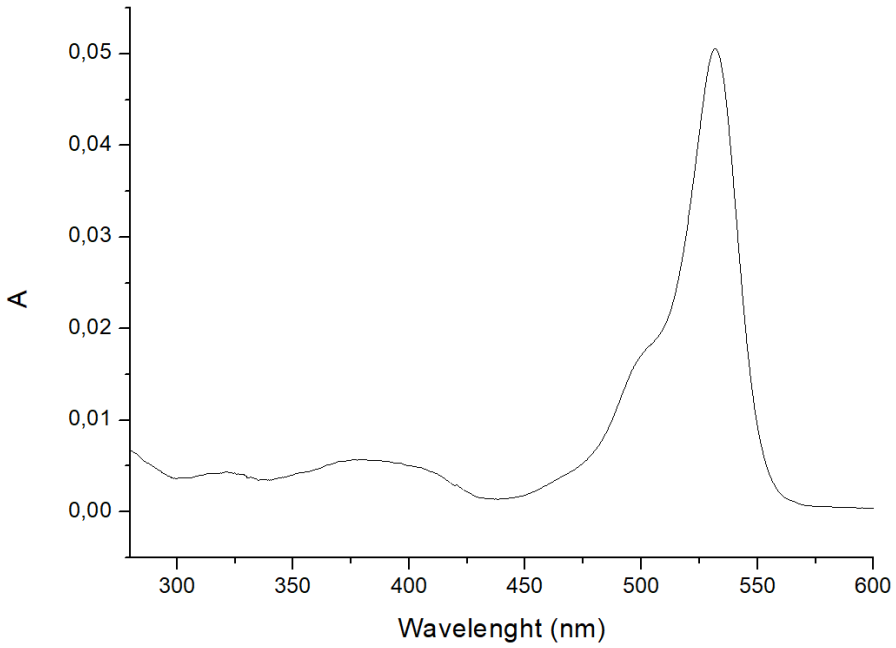


Figure S4. UV-Vis spectrum of **BDPy-NH_2-AE** in $CHCl_3$ (1 x 10^{-6} M)

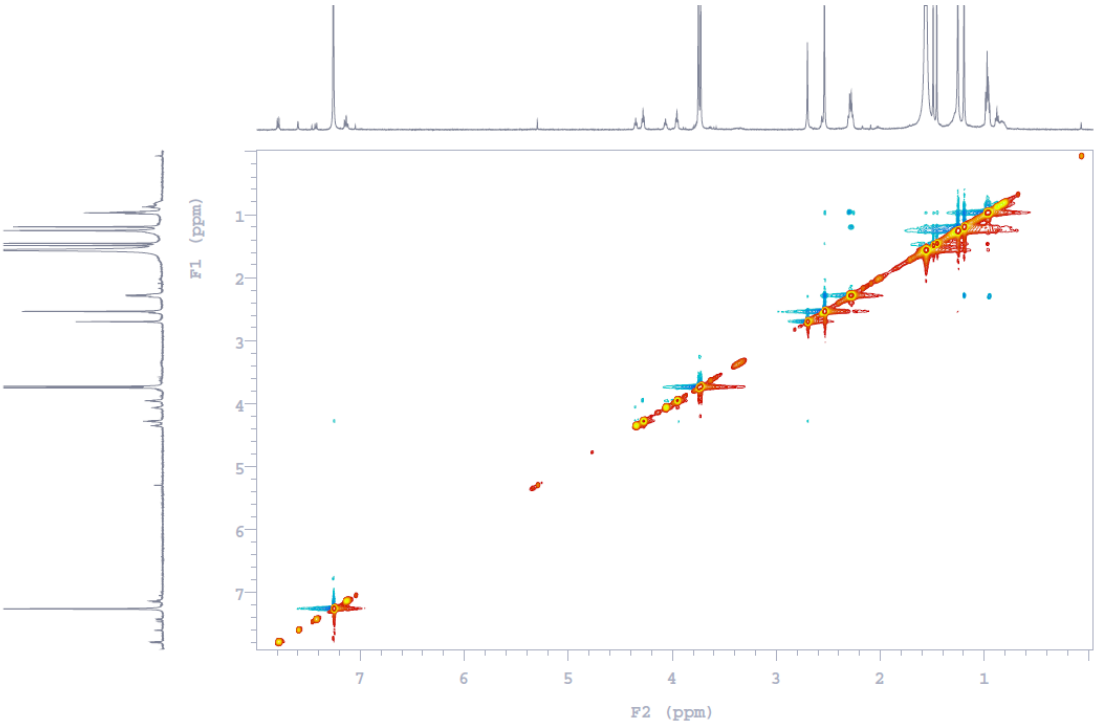
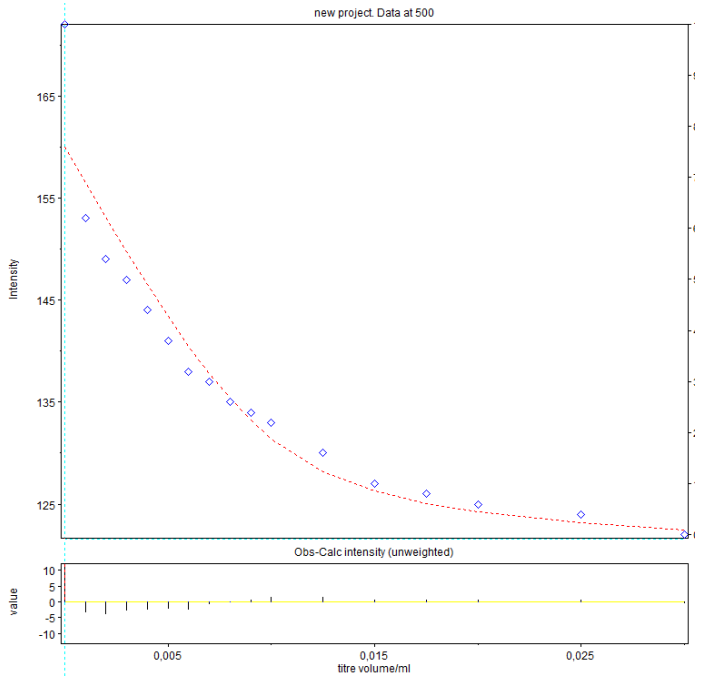


Figure S5. ROESY spectrum of supramolecular complex between **BDPy-NH_2-AE** and DMMP ([**BDPy-NH_2-AE**] = [DMMP] = 1 x 10^{-3} M in $CDCl_3$).

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Converged in 1 iterations with sigma = 3,615
                      standard
Log beta    value     deviation
AB          7.0905    0.4351
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Figure S6. HypSpec plot and output file of fluorescence titration between **BDPy-NH_2-AE** and DMMP

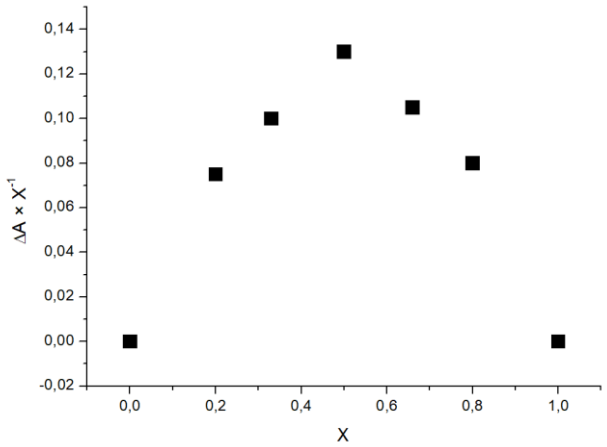

Figure S7. Job's plot of supramolecular complex between **BDPy-NH$_2$-AE** and DMMP

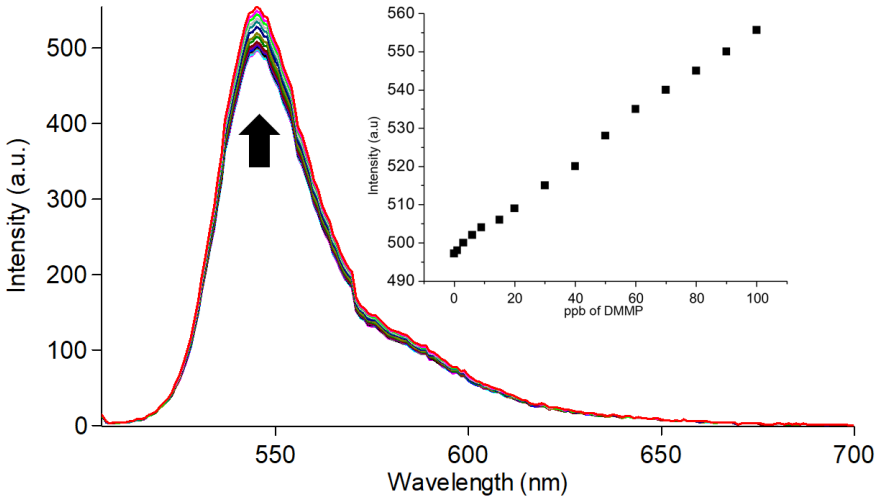

Figure S8. Fluorescence titration between **BDPy-NH$_2$-AE** ($CHCl_3$, 1 x 10^{-6} M, λ_{exc} 480 nm) and DMMP (0-100 ppb), inset shows the plot of emissions recorded at 545 nm.

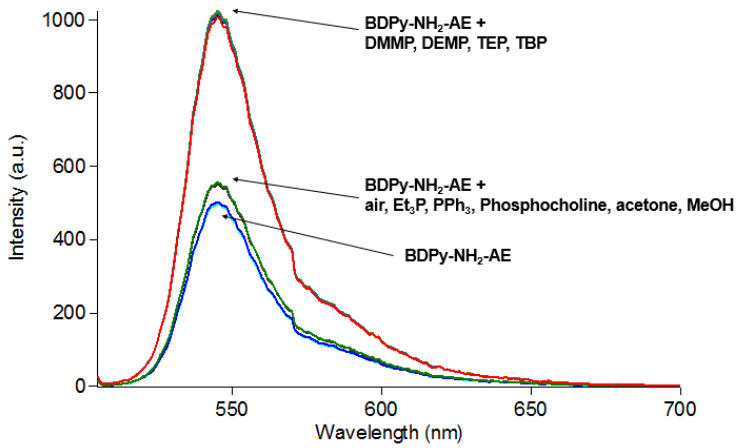

Figure S9. Selectivity test: emission spectra of **BDPy-NH$_2$-AE** solution (1×10^{-6} M in $CHCl_3$, λ_{ex} = 480 nm,) after the exposure to air (bubbled for 5 min), other competitive guests (10 eq.), and DMMP, DEMP, TEP and TBP (1 equiv.).

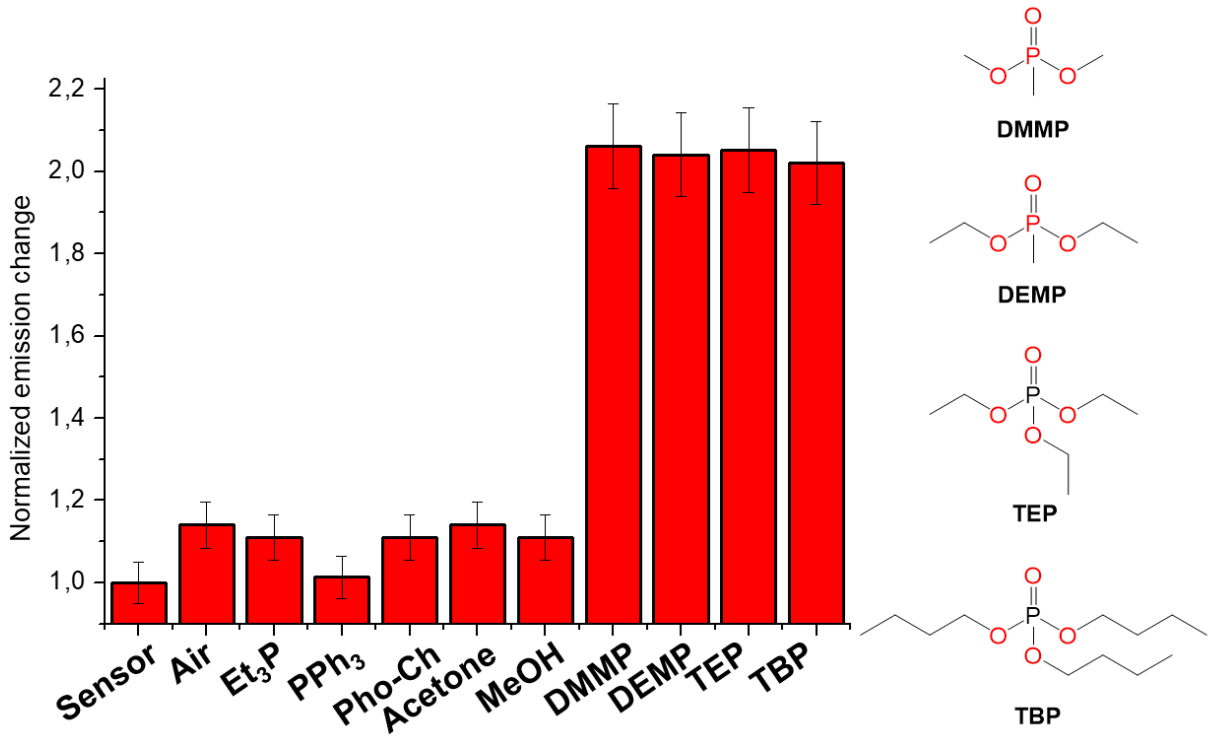

Figure S10. Selectivity tests: Normalized emission change of **BDPy-NH$_2$-AE** solution (I/I_0, 1×10^{-6} M in $CHCl_3$, λ_{ex} = 480 nm, λ_{em} = 540 nm) after the exposure to air (bubbled for 5 min), other competitive guests (10 eq.), and DMMP, DEMP, TEP and TBP (1 equiv.), highlighting in red the H-bond acceptor sites.

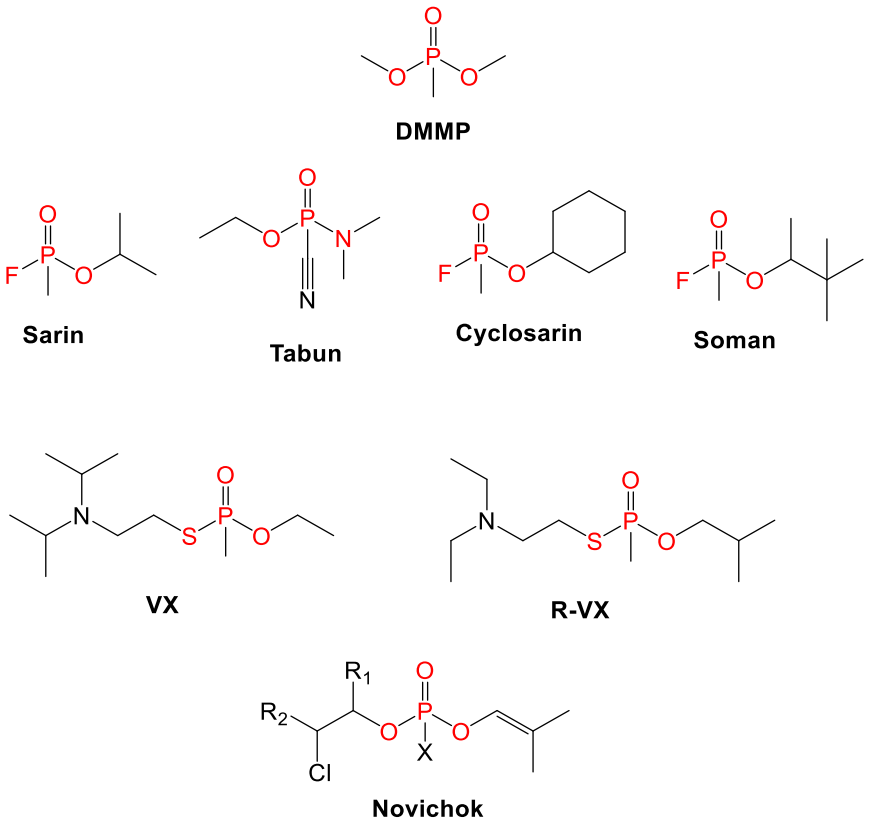

Figure S11. Chemical structures of organophosphorus Nerve Agents and DMMP simulant, highlighting in red the atoms involved in the supramolecular recognition by **BDPy-NH$_2$-AE**