

VX and VG chemical warfare agents bidentate complexation with lanthanide ions

Genevieve H. Dennison, Mark R. Sambrook and Martin R. Johnston

Supporting information

Reagents:

VX and VG were synthesised in-house and were > 95% pure. All non-CWA reagents and solvents were obtained from Sigma-Aldrich (Australia) and were used as received without further purification.

Solvents:

DMF was distilled under nitrogen and stored over sieves before use. Acetonitrile was purchased dry from Sigma-Aldrich (Australia).

Synthesis:

Lanthanide complexes [Eu(phen)₂(NO₃)₃(H₂O)₃] and [Tb(phen)₂(NO₃)₃(H₂O)₂] were prepared using a modification of the literature procedures^[1] and were characterised by elemental and IR analyses.^[2]

Elemental

[Eu(phen)₂(NO₃)₃(H₂O)₃]: Found C 38.37%, H 2.60%, N 12.79% calculated Eu(phen)₂(NO₃)₃·(H₂O)₃ C 38.31%, H 2.95%, N 13.03%.

[Tb(phen)₂(NO₃)₃(H₂O)₂]: Found C 39.27%, H 2.43%, N 12.96% calculated Tb(phen)₂(NO₃)₃·(H₂O)₂ C 39.25%, H 2.74%, N 13.35%.

IR

[Eu(phen)₂(NO₃)₃(H₂O)₃]: 1626 (C=C, C=N), 1590 (C=C, C=N), 1578 (C=C, C=N), 1519, 1495 (ν₄ NO₃⁻), 1462, 1424 (C=C, C=N), 1307 (ν₁ NO₃⁻), 1271 (C=C, C-H), 1143, 1103 (C-H in plane), 1035 (ν₂ NO₃⁻), 1027, 864 (C-H out of plane), 848 (C-H out of plane, C-N), 815 (ν₆ NO₃⁻), 773 (C-H out of plane), 738 (ν₃ NO₃⁻), 723 (C-H out of plane).

[Tb(phen)₂(NO₃)₃(H₂O)₂]: 1626 (C=C, C=N), 1590 (C=C, C=N), 1578 (C=C, C=N), 1520, 1496 (ν₄ NO₃⁻), 1463, 1424 (C=C, C=N), 1312, 1273 (C=C, C-H), 1222 (C=C, C-H), 1210 (C=C, C-H), 1144, 1104 (C-H in plane), 1037 (ν₂ NO₃⁻), 1029, 865 (C-H out of plane), 848 (C-H out of plane, C-N), 816 (ν₆ NO₃⁻), 741 (C-H out of plane), 741 (ν₃ NO₃⁻), 724 (C-H out of plane).

Instrumentation

Solution fluorescence studies were performed on an OceanOptics portable USB 2000 fluorimeter with fibre optic cables and PX-2 pulsed xenon light source (Integration Time (μsec): 100000, Spectra Averaged: 10, Boxcar Smoothing: 0).

UV-Vis studies were performed on a Thermo Scientific Evolution 201 UV-Vis spectrophotometer (absorbance, band width = 2nm, Integration time 0.05 seconds, data interval 1.00 nm, scan speed 1200 nm/min).

IR spectra (ATR) were obtained on a Perkin Elmer FT-IR Frontier spectrometer (scan rate 4, resolution 4cm⁻¹, diamond ZnSe).

General titration methodology

Solutions of the lanthanide complexes ($1 \times 10^{-3} \text{ mol dm}^{-3}$) were prepared in dry dimethylformamide / dry acetonitrile (1:9) before dilution to $1 \times 10^{-5} \text{ mol dm}^{-3}$ in acetonitrile. Diluted solutions of the complexes were prepared fresh each day from the $1 \times 10^{-3} \text{ mol dm}^{-3}$ stock solutions before titration. Blank additions of acetonitrile were performed to account for any fluorescence changes resulting from concentration differences.

Guest (CWA and simulant) solutions were prepared in dry acetonitrile and added to the lanthanide complex solution in a septa fitted cuvette. The concentration of the guest solution was varied during the course of the titrations to ensure $[H_{\text{initial}}]$ was as close to $[H_{\text{final}}]$ as possible. The solution was left stirring without irradiation for at least 2 minutes after each addition of guest before a spectrum was obtained.

Spectral plots

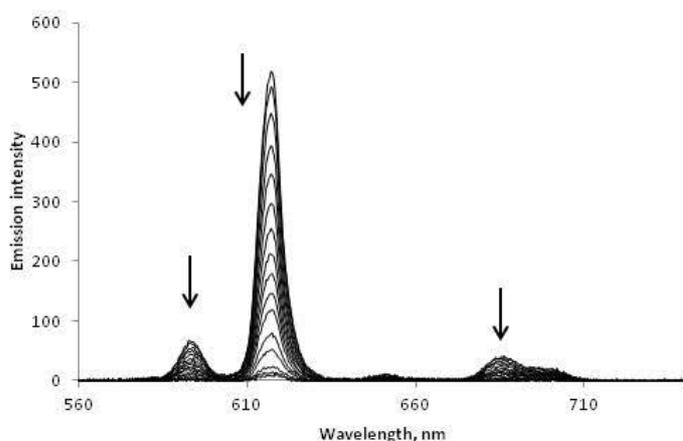


Figure S1. Quenching of the luminescent emission of **1** upon addition of VG; $[\text{complex}] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, 293K.

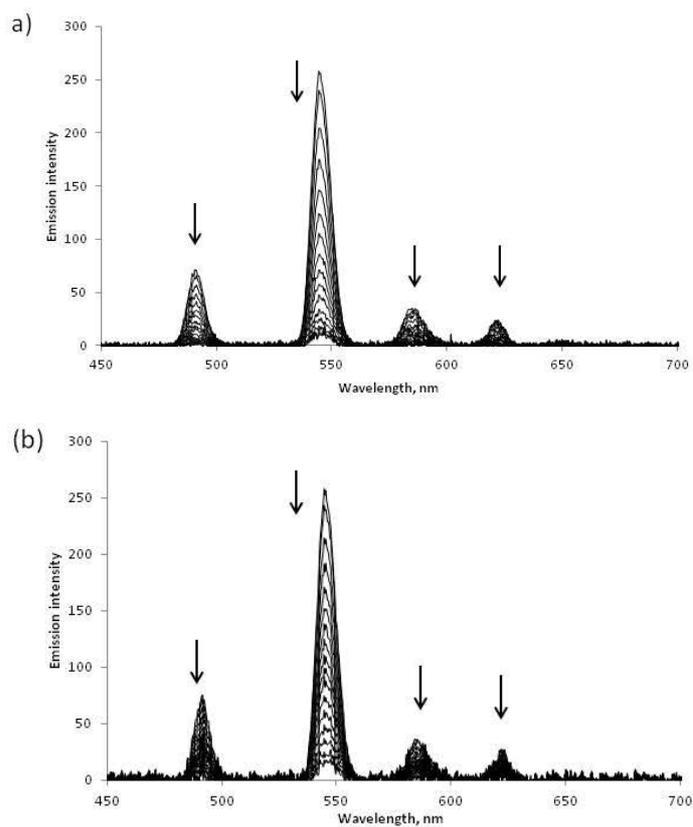


Figure S2. Quenching of the luminescent emission of **2** upon addition of (a) VX and (b) VG; [complex] = 1×10^{-5} mol dm⁻³, 293K.

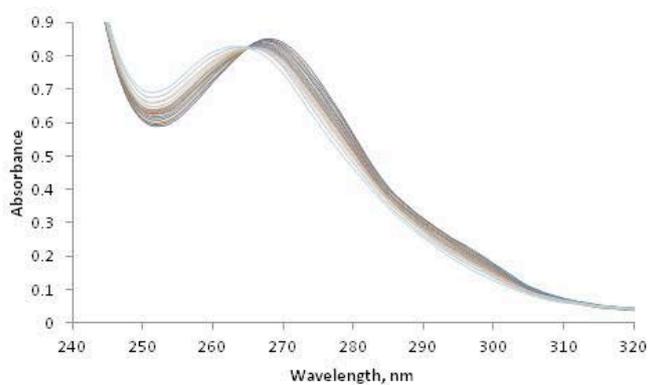


Figure S3. UV-Vis titration data for the addition of VG to **1**; [complex] = 1×10^{-5} mol dm⁻³, 293 K.

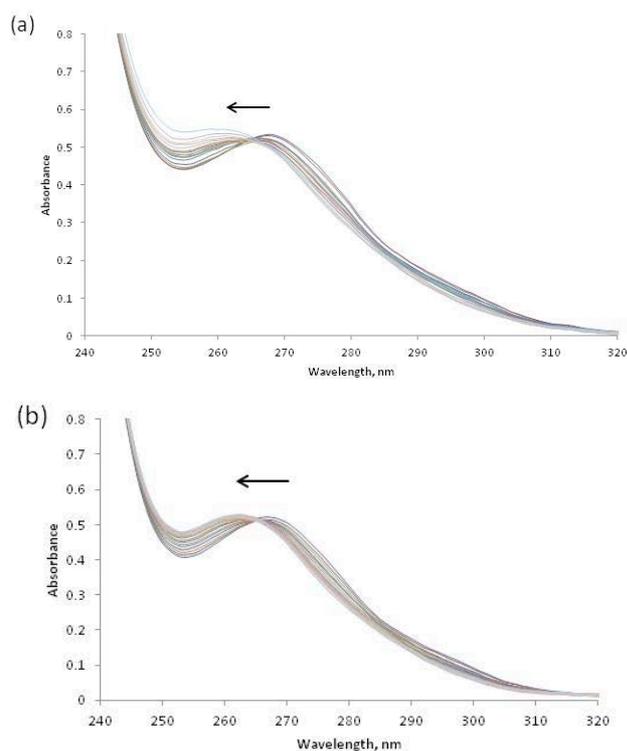


Figure S4. UV-Vis titration data for the addition of (a) VX and (b) VG to **2**; [complex] = 1×10^{-5} mol dm⁻³, 293 K.

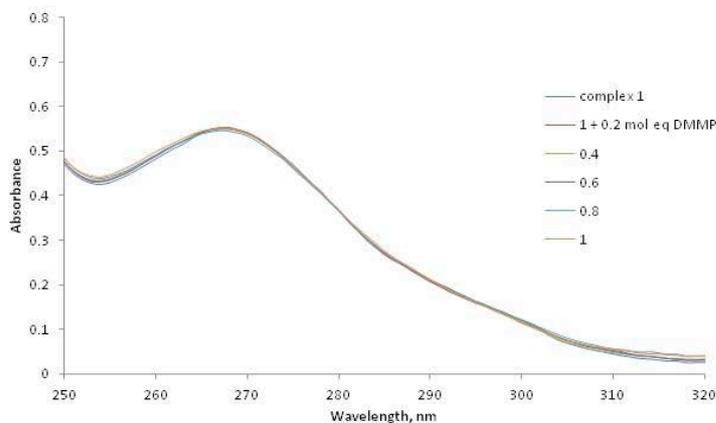


Figure S5. Selected UV-Vis spectral data from the titration of **1** with DMMP; [complex] = 1×10^{-5} mol dm⁻³, 293 K.

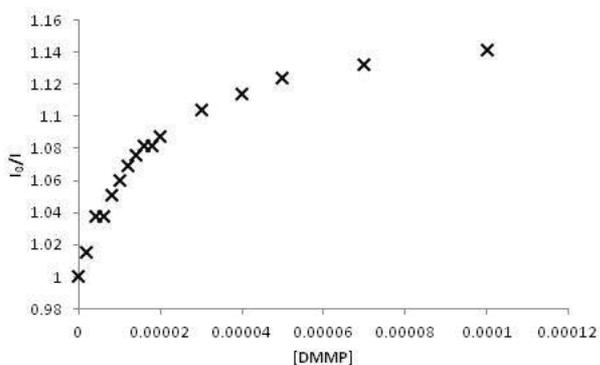


Figure S5. Stern-Volmer plot of the luminescent quenching titration of **1** with DMMP up to 10 mol equivalents of DMMP added where $\lambda^{em} = 617$ nm; [complex] = 1×10^{-5} mol dm⁻³, 293 K.

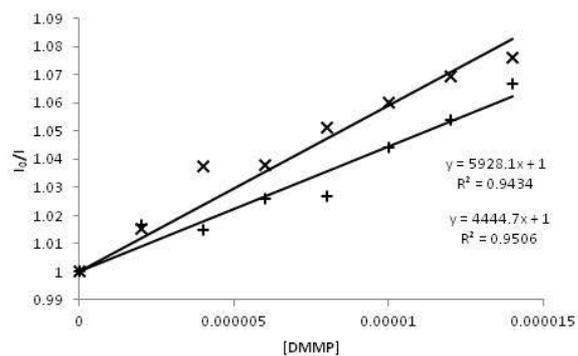


Figure S6. Fitting of low quencher concentration region of the Stern-Volmer plot for the titration of **1** with DMMP (two titration data sets shown); $[complex] = 1 \times 10^{-5} \text{ mol dm}^{-3}$, 293 K.

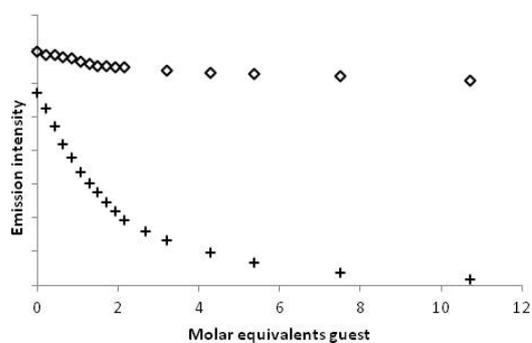


Figure S7. Comparison of the luminescence emission quenching of **1** by VX (+) and DMMP (\diamond) where $\lambda^{em} = 617 \text{ nm}$; $[complex]_{initial} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, 293 K.

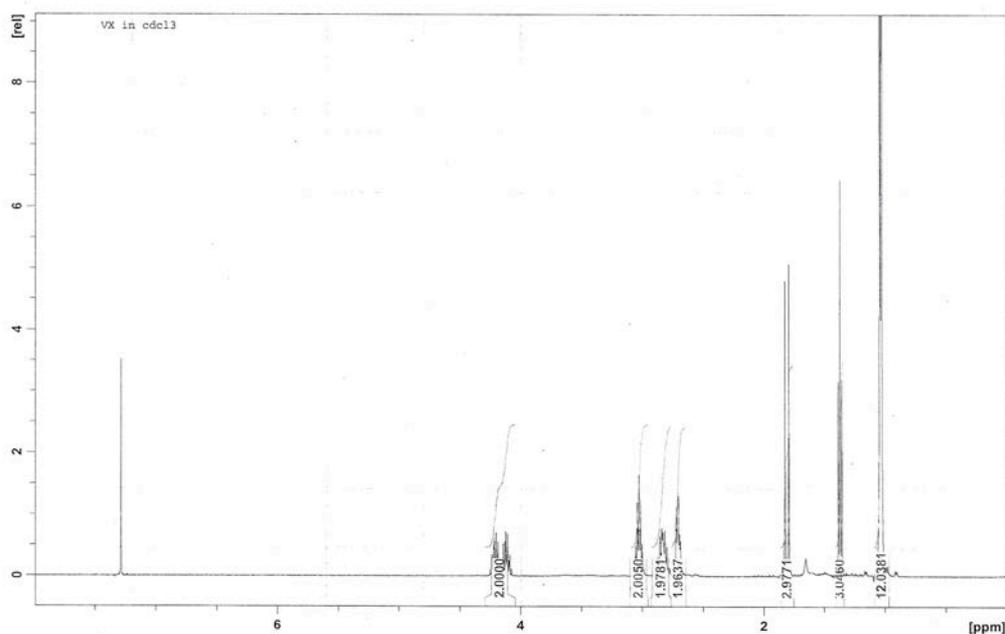


Figure S8. ^1H NMR spectrum of the VX used in this study (CDCl_3)

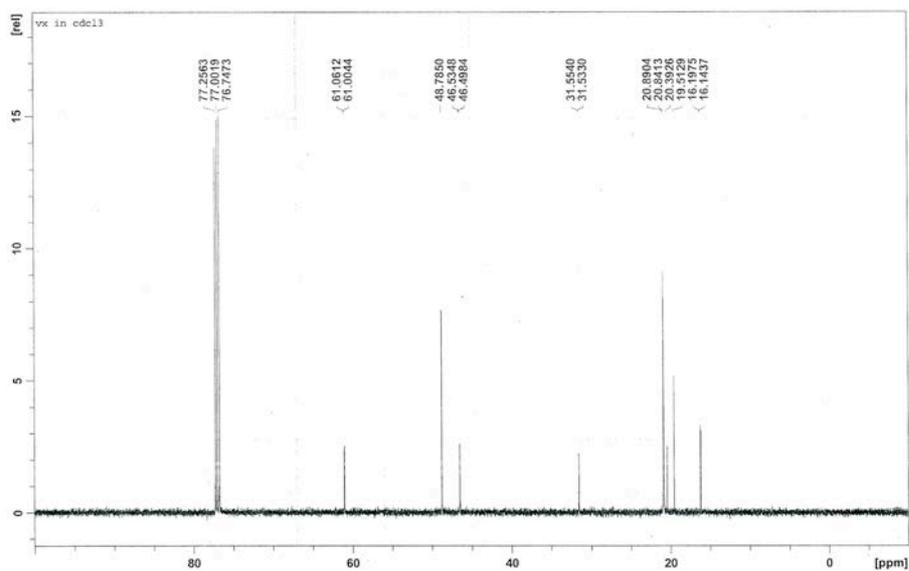


Figure S9. ^{13}C NMR spectrum of the VX used in this study (CDCl_3)

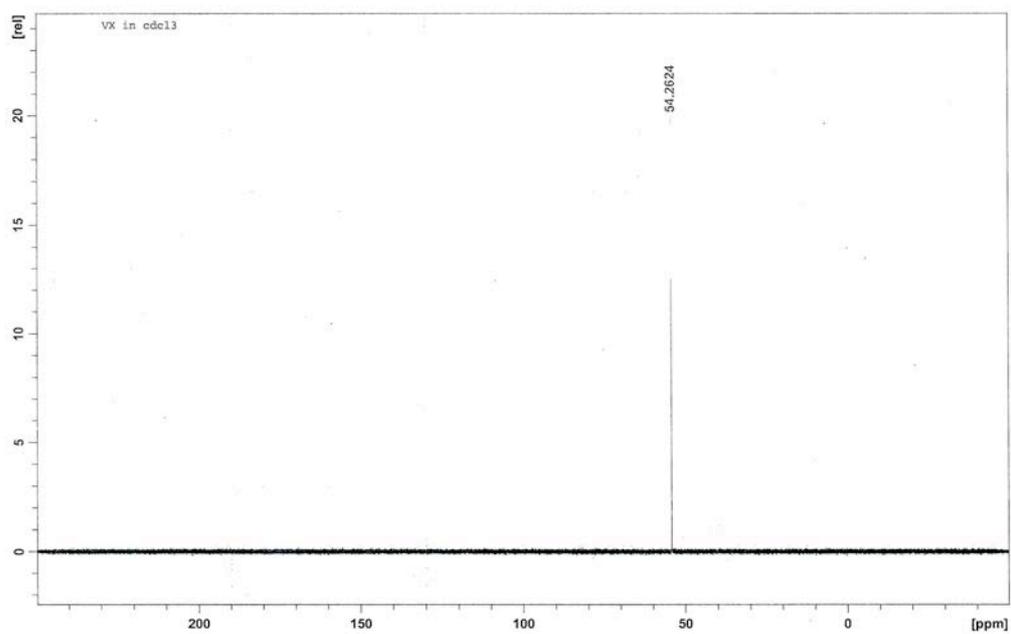


Figure S10. ^{31}P NMR spectrum of the VX used in this study (CDCl_3)

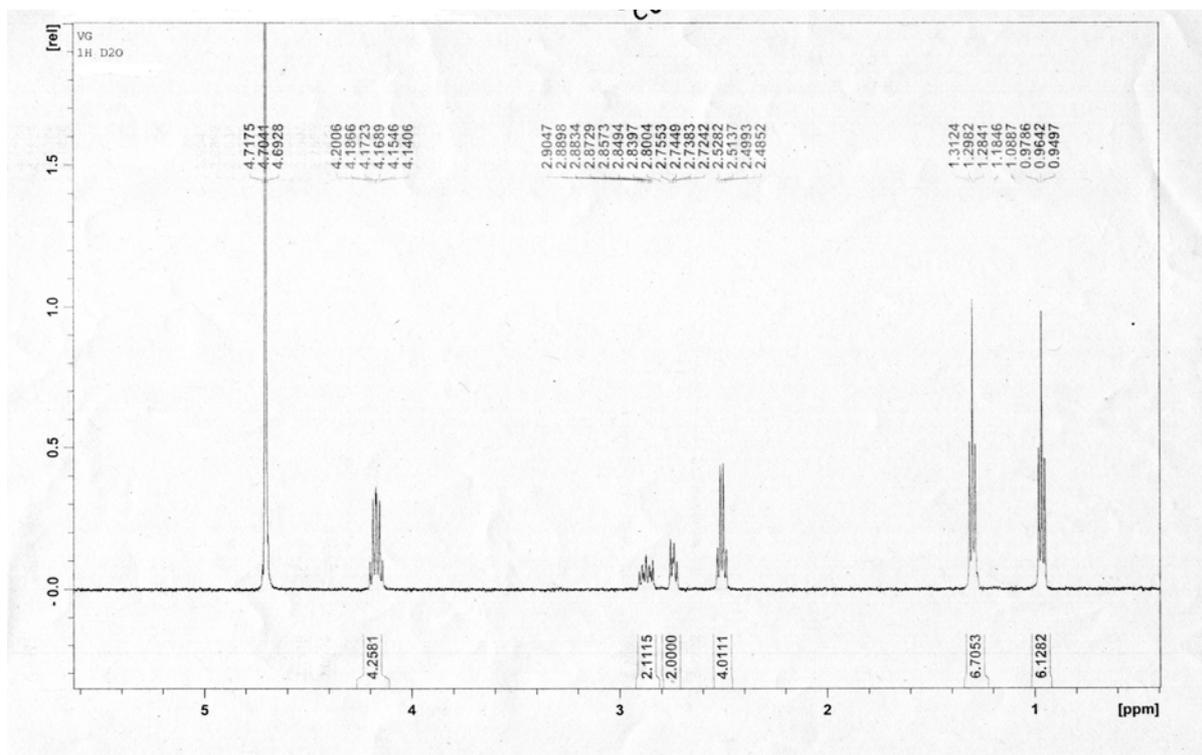


Figure S11. ^1H NMR spectrum of the VG used in this study (D_2O)

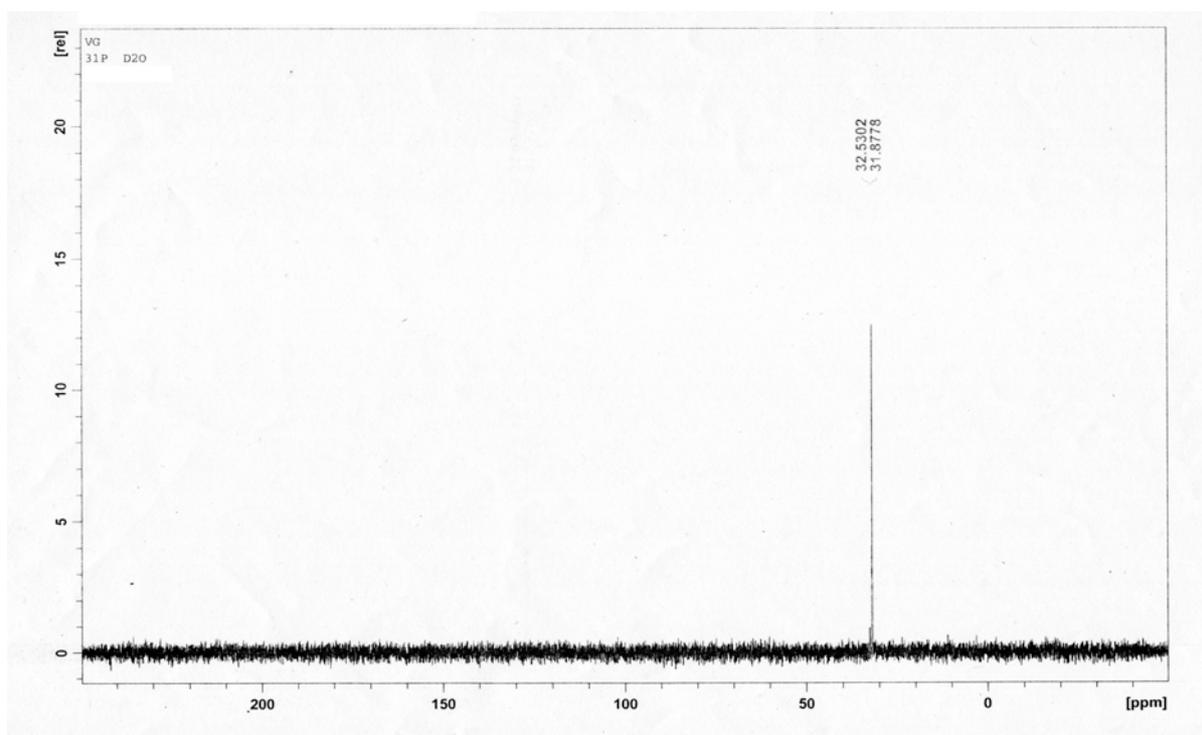


Figure S12. ^{31}P NMR spectrum of the VG used in this study (D_2O)

References

- [1] R. C. Grandey, T. Moeller, *J. Inorg. Nucl. Chem*, **1970**, 32(1): 333-336.
- [2] V. Tsaryuk, V. Zolin, L. Puntus, V. Savchenko, J. Legendziewicz, J. Sokolnicki, R. Szostak, *J. Alloy. Compd.*, **2000**, 300-1, 184-192.

