

Supplementary Information

Influence of the secondary ligand, phenanthroline, on the antioxidant and pro-oxidant and cytotoxic effects of the oxidovanadium(IV)/naringin complex

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Experimental Section

Spectrophotometric method for the determination of V content

Tungstophosphovanadate(V) was obtained as a result of the reaction of vanadium(V) in acidic solution with phosphoric acid and sodium tungstate. Briefly, a solid sample (15–20 mg) was subjected to acid digestion by adding a mixture of sulfuric acid and nitric acid in a 3:1 ratio, followed by heating. This process was repeated 3 to 5 times with the intention of destroying all organic matter and oxidizing vanadium. Subsequently, 5 mL of 50% v/v phosphoric acid and 5 mL of 10% p/v sodium tungstate were added to the digested sample. The mixture was heated to 100 °C for 15 min and then brought to a final volume of 50 mL with distilled water. The absorbance of the solution was measured at 400 nm, and the vanadium content was determined by comparing the results with a previously prepared calibration curve using NH_4VO_3 .

Method for the general experiments

Elemental analysis is a technique that allows determining the major elements of an organic substance, namely carbon, hydrogen, nitrogen, and sulfur. This is commonly done using commercial analyzers where the sample undergoes oxidative decomposition, forming the final products: carbon dioxide, water, nitrogen, and sulfur dioxide. The separation of the gases is carried out through gas chromatography with a variable-length Porapac column, and thermal conductivity detection is employed for detection. The method necessitates prior calibration with a substance of known composition. In our case, two standards were used: one of BBOT (2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene) and the other of sulfanilic acid.

Thermal analysis refers to the study of a material's behavior as a function of its temperature, in the atmosphere of a specific gas or in a vacuum. In thermogravimetric analysis (TGA), the mass of a sample is recorded while the temperature is increased over time, providing information about the thermal stability of the compound.

Generally, TGA allows for the determination of the presence of water or solvent molecules directly coordinated to the metal or solvated molecules. Through analyzing the percentage of residue mass obtained and characterizing it, the stoichiometry of the complex can be inferred.¹

The absorption and emission spectra resulting from the vibrational and rotational movements of a non-electronically excited molecule are primarily found in the infrared region. Infrared spectroscopy is a technique used to analyze the vibrational modes of molecules measuring the interaction of the infrared radiation with matter. The functional groups present in molecules can be identified through infrared absorption bands that are characteristic of each group. These bands correspond to the fundamental vibrations of the functional groups. The shifts of these bands upon metal coordination are indicative of the metal-ligand interaction.^{2,3}

UV-Vis spectrophotometry is a widely used analytical method that measures the absorption of light in the ultraviolet-visible spectral region (200-800 nm) by a sample. The detected absorption is due to the promotion of electrons to an excited energy state. Electrons in different environments within a substance require a specific amount of energy to be promoted to a higher energy state, and thus substances absorb light at different wavelengths, which is detected as the absorbance peak. The absorbance of the sample is proportional to the concentration of the compound. For solid samples, in the same spectral region, diffuse reflectance UV-Vis spectroscopy is a widely used technique for the analysis of powders and surfaces. The technique is based on directing a collimated UV-Vis radiation beam at a specific angle onto the sample, and as a result, the surface reflects the radiation. The obtained value is converted into reflectance (relative reflectance) with respect to the reflectance of the reference standard.⁴

Fluorescence and phosphorescence are forms of luminescence and consist of the emission of light from a substance, typically from UV-Vis spectral range, from electronically excited states. The sample absorbed light and the electron is promoted

to an excited state. When it returned to the ground state, in most cases, the fluorescent emission of the photon occurs at longer wavelength with a lower photon energy. ⁵

Electron Paramagnetic Resonance (EPR) spectroscopy is used to measure the absorption of radiation in the microwave region (104–106 MHz) by substances containing one or more unpaired electrons (paramagnetic). Paramagnetic substances exhibit EPR spectra under the influence of an applied magnetic field, through their interaction with unpaired electrons. ⁶

The Inductively Coupled Plasma (ICP-MS) is an ionization source that transforms the elements of a sample into ions. It uses a plasma source of Ar to generate ionization state for elements. For the separation of ions, it uses a mass spectrometer (MS) in parallel with a quadrupole mass filter. Inductively Coupled Plasma (ICP) has become the dominant source for rapid multielement spectroscopic analysis due to its attributes, including low detection limits, a broad linear dynamic range, and high precision. It is a method that allows the simultaneous determination of all metallic elements and offers several advantages over atomic absorption techniques, such as complete atomization, a virtually radiation-free plasma background, and minimal ionization or self-absorption interferences. ⁷

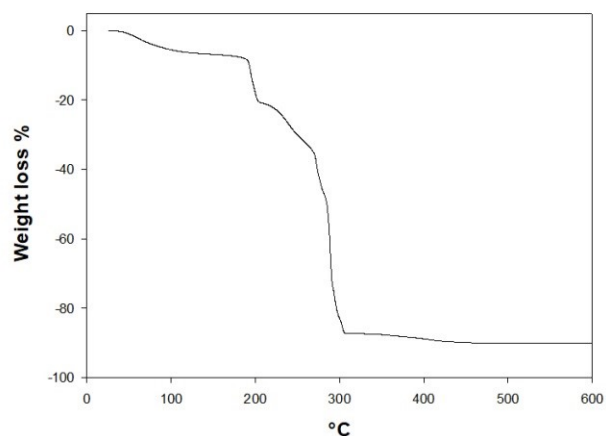


Figure S1. Thermogravimetric analysis (TGA) curve for the thermal decomposition of $[\text{VONargPhenCl}]\cdot 3\text{H}_2\text{O}$. Oxygen flow: 50 mL/min, rate: $10^\circ\text{C}/\text{min}$.

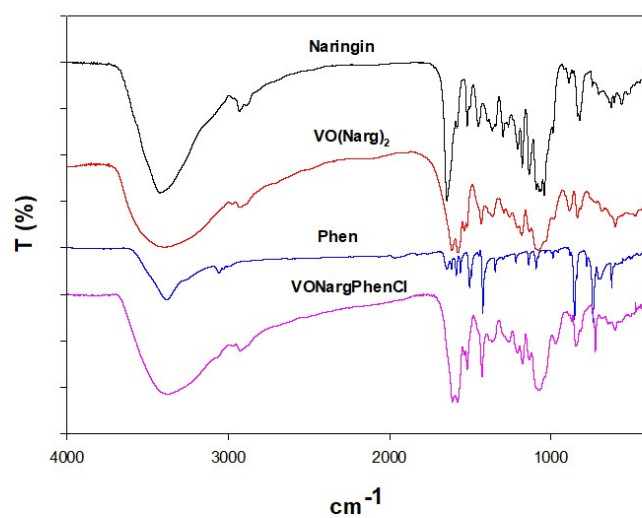
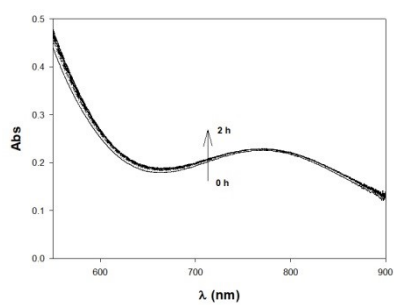
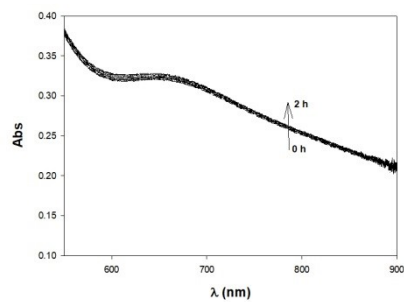


Figure S2. Infrared spectra of naringin, $[\text{VO}(\text{Narg})_2]\cdot 8\text{H}_2\text{O}$, 1,10-Phenanthroline and the ternary complex $[\text{VONargPhenCl}]\cdot 3\text{H}_2\text{O}$



DMSO



1 % DMSO-99 % H₂O

Figure S3. Electronic spectra of VONargPhenCl complex in (2.5×10^{-3} M, DMSO) and (2.5×10^{-3} M, 1 % DMSO-99 % H₂O) during 2 h, 25 °C.

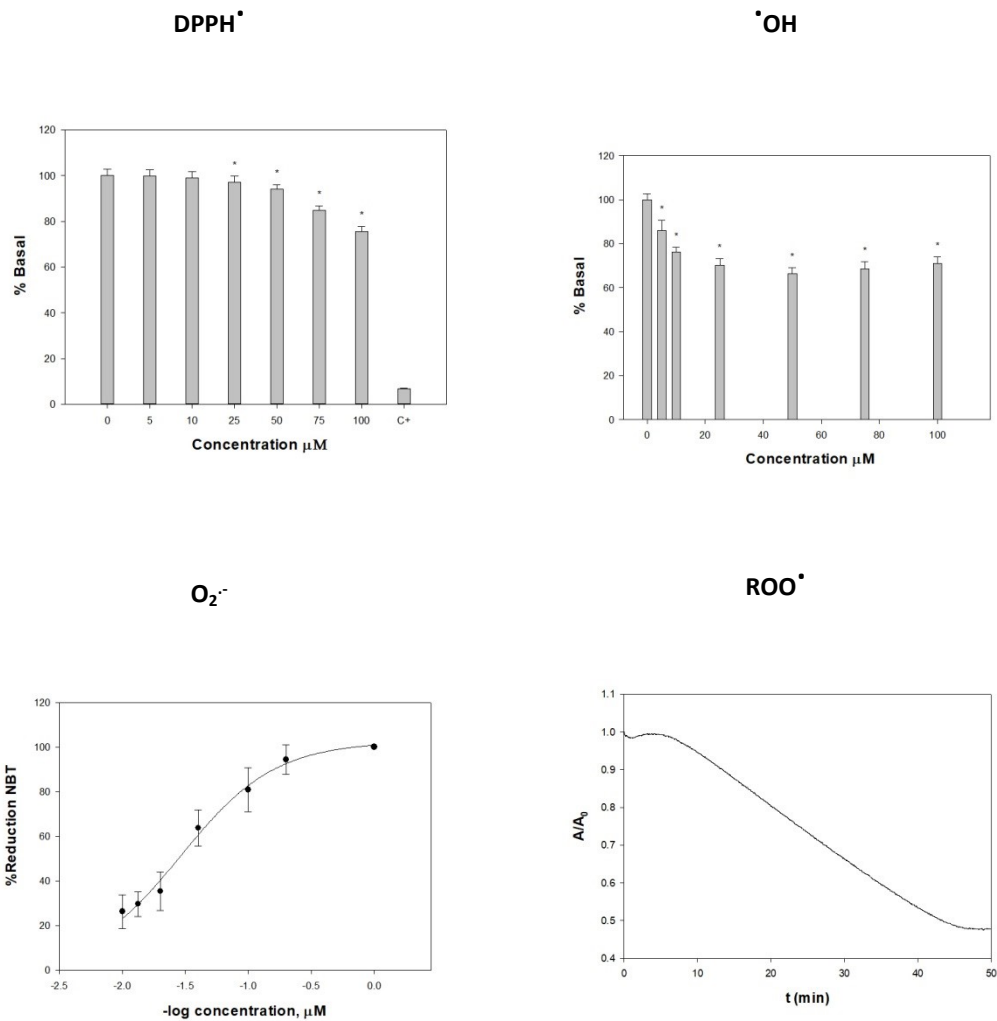


Figure S4. Effects of VONargPhenCl on: DPPH[•], the reduction in the concentration of DPPH[•] radical (517 nm); •OH, the development of a pink chromogen ($\lambda = 532$ nm) from the reaction of deoxyribose, hydroxyl radicals and thiobarbituric acid (TBA); O₂^{•-}, the reduction of nitroblue tetrazolium by the generated superoxide radical at 560 nm; ROO[•], AAPH-generated peroxy radicals-pyranine mixture. Time delay (lag phase) of pyranine consumption, measured at 454 nm. The values are expressed as the mean \pm SEM of at least three independent experiments.

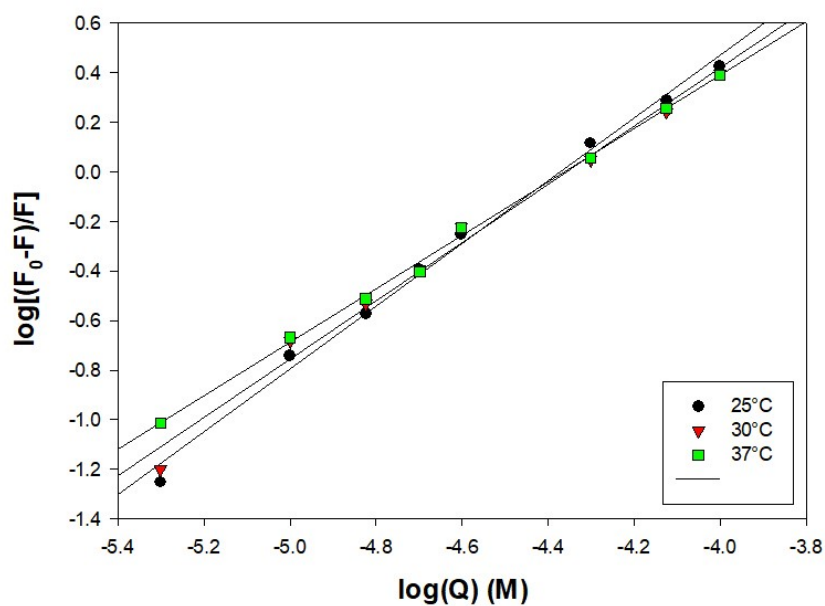


Figure S5. Plots of $\log [(F_0-F)/F]$ vs $\log (Q)$ for the interaction of BSA with VONargPhenCl at different temperatures, $\lambda_{\text{ex}} = 280 \text{ nm}$.

References

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