Supplementary material

Synthesis, Characterization, and In Vitro Insulin-Mimetic Activity Evaluation of Valine Schiff Base Coordination Compounds of Oxidovanadium(V)

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1. **Methods**

The Stern–Volmer equation

The Stern–Volmer equation [1] is:

$$I_0/I = 1 + K_q\tau_0[Q] = 1 + K_{sv}[Q],$$

where: I_0 = the fluorescence intensities of free BSA solution at 347 nm,

I = the fluorescence intensities of BSA solution at 347 nm in the presence of vanadium complexes,

[Q] = the concentration of vanadium complexes,

τ_0 = the fluorescence lifetime of the biopolymer (10^{-8} s),

K_q = the collision quenching constant;

K_{sv} = the Stern-Volmer constant.

Stern–Volmer plots of the BSA fluorescence quenching in the presence of each compound are represented in Fig. S4, together with their linear best fit in which $y = I_0/I$, $x = [Q]$, a = slope of the line, and b = y-intercept. The plots exhibit a good linear relationship with R^2 between 0.9794 and 0.9965. The fluorescence intensities are the average of three recordings measured at a scanning speed of 250 nm/min, with an excitation and emission bandwidth of 5 nm.

2. Results
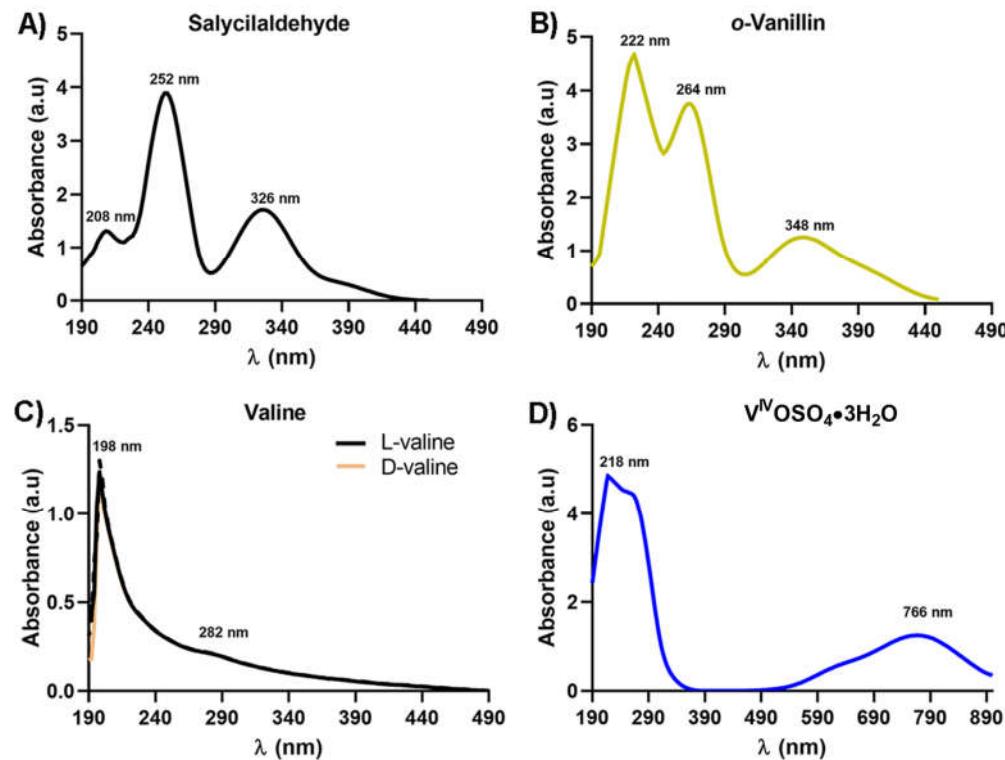
Figure S1. Absorption spectra of 5×10^{-4} M salicylaldehyde (**A**), *o*-vanillin (**B**), 2×10^{-3} M D-/L-valine (**C**), and 7.2×10^{-2} M V^{IV}OSO$_4 \cdot 3$H$_2$O (**D**) in phosphate-buffered saline (PBS) at pH 7.4.
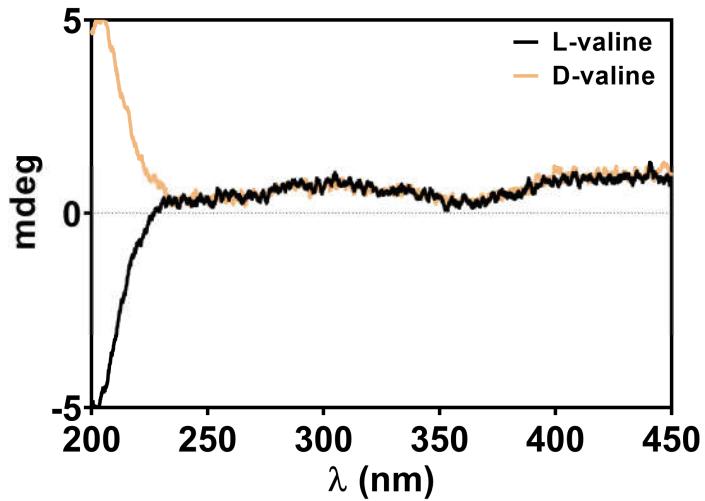

Figure S2. CD spectra of 2×10^{-2} M L-/D-valine in phosphate-buffered saline (PBS) at pH 7.4.
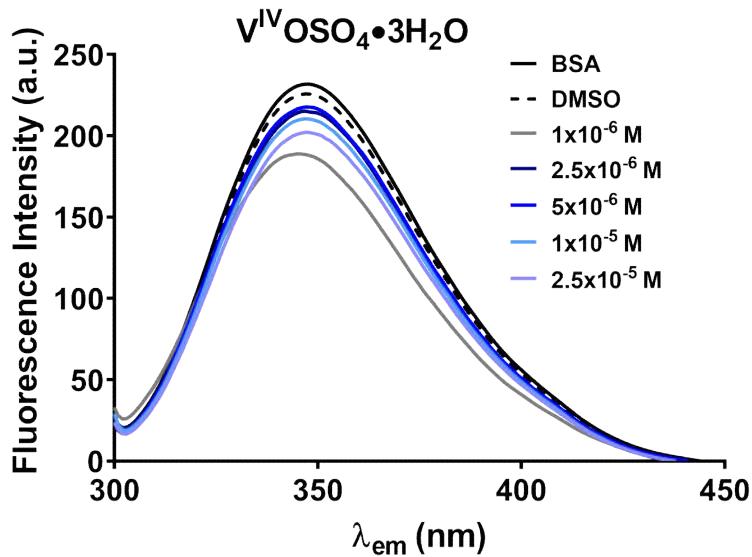
Figure S3. Fluorescence spectra of the 2×10^{-6} M BSA in phosphate-buffered saline (PBS) at pH 7.4, in the presence of various concentrations (1-25×10^{-6} M) of $V^{IV}OSO_4 \bullet 3H_2O$.
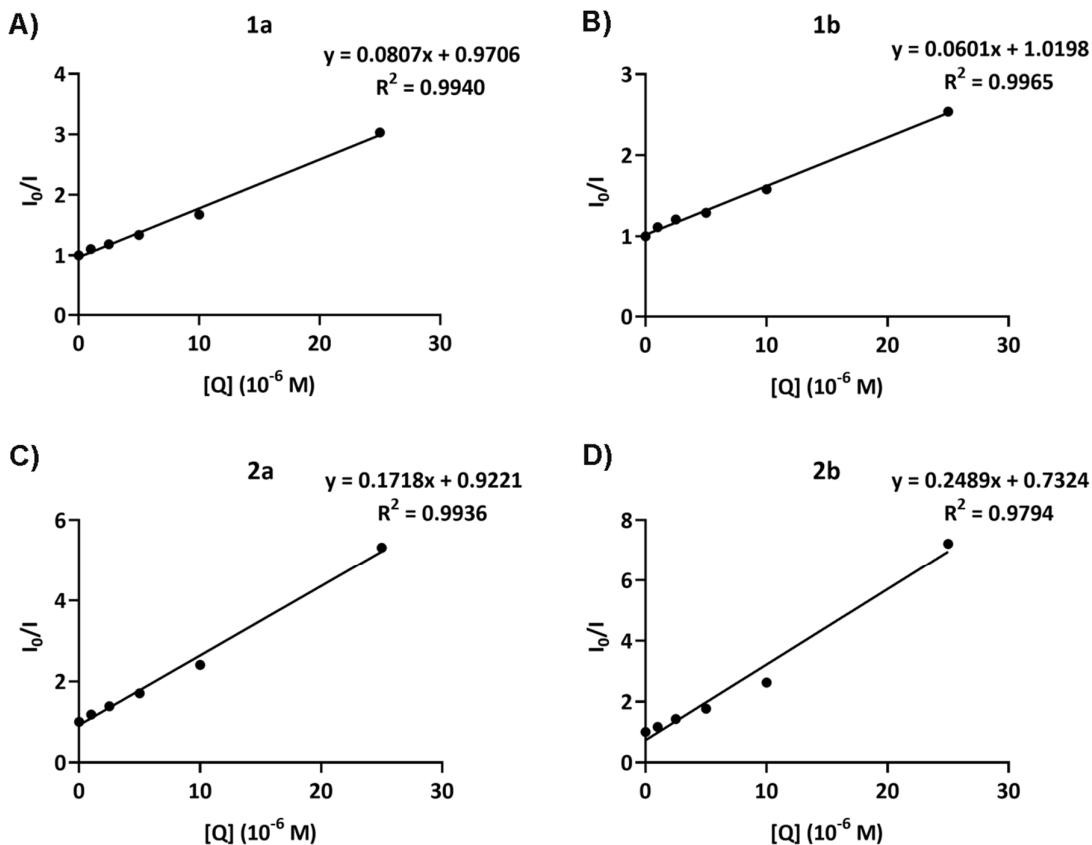

Figure S4. The plots of I_0/I *vs.* [Q] for 1a (**A**), 1b (**B**), 2a (**C**), and 2b (**D**).

Table S1. The main infrared absorption frequencies (cm^{-1}) corresponding to various groups for 1a, 1b, 2a, and 2b complexes.

ν (cm^{-1})	1a	1b	2a	2b
νO-H	3703	3701	3702-3400	3702-3400
νC-H methyl	2966-2870	2966-2870	2966-2872	2966-2872
νC=N	1712-1683	1712-1683	1680	1680
ν_{as}COO$^-$	1602	1602	1627	1627
νC=C	1554	1554	1570	1570
ν_sCOO$^-$	1394	1394	1411	1411
νC$_{Ph}$-O	1286	1286	1259	1259
νV=O	991	991	974	974
ν_{as}(V-O-V)	761	761	744	744
νV–N	571	571	597	597
νV–O	451	451	459	459

Table S2. The main infrared absorption frequencies (cm^{-1}) corresponding to various groups in the precursors of oxidovanadium(V) complexes.

ν (cm^{-1})	**Valine**	**Salicylaldehyde**	*o*-Vanillin
νO-H	3160	3064	3015
νC-H methyl	2958	-	2973
νN-H	2625-2110	-	-
νC=O	-	1664	1639
ν_{as}COO$^-$	1612	-	-
νC=C	-	1487	1455
ν_sCOO$^-$	1323	-	-
νO-H	-	1386	1389
νC$_{Ph}$-O	-	1276	1259

Table S3. The crystallographic data of 1a and 2a.

Compound	1a	2a
Formula	C$_{48}$H$_{56}$N$_4$O$_{20}$V$_4$	C$_{28}$H$_{34}$N$_2$O$_{13}$V$_2$
Formula weight/ g mol^{-1}	1212.72	710.47
T/K	293(2)	293(2)
λ/Å	0.71073	0.71073
Crystal system	Hexagonal	Monoclinic
Space group	P6$_1$	C2
Unit cell		
a/Å	14.5093(2)	23.399(5)
b/Å	14.5093(4)	9.4811(19)
c/Å	45.9511(4)	7.4902(15)
α/deg	90	90
β/deg	90	92.67(3)
γ/deg	120	90
V/Å^3	8377.6(2)	1659.9(6)
Z	6	2
Calculated density/g cm^{-3}	1.442	1.421
Absorption coefficient/cm^{-1}	0.724	0.627
F(000)	3744	736
Crystal size/mm × mm × mm	0.24 x 0.12 x 0.09	0.4 x 0.2 x 0.1
θ range/deg	1.621 to 24.508	2.318 to 24.999
Limiting indices	-16 < h < 16, -16 < k < 16 -53 < l < 49	-27 < h < 27, -10 < k < 11, -8 < l < 8

Collected reflections	36236	4602
Symmetry independent reflections	9016	2453
Rint	0.0583	0.1662
Data/restraints/ parameters	9016 / 13 / 696	2453 / 1 / 204
GOF on F2	1.064	1.132
Final R indices	R1 = 0.0573 wR2 = 0.1502	R1 = 0.0832 wR2 = 0.1882
Largest diff peak and hole/e Å^{-3}	0.546 and -0.342	0.613 and -0.515
Flack parameter	0.01(2)	0.06(13)

Table S4. Summary of IC_{50} values (M) calculated for 1a, 1b, 2a, 2b, $V^{IV}OSO_4\bullet 3H_2O$, and cisplatin from dose-response cytotoxicity data generated by XTT assay, measuring the viability of HepG2 cells exposed for 24 hours to the compounds.

Compound	IC_{50} (M) ± SD (M)
1a	$2.3 \times 10^{-4} \pm 2.4 \times 10^{-5}$
1b	$2.0 \times 10^{-4} \pm 4.3 \times 10^{-5}$
2a	$2.3 \times 10^{-4} \pm 2.2 \times 10^{-5}$
2b	$2.3 \times 10^{-4} \pm 2.9 \times 10^{-5}$
$V^{IV}OSO_4\bullet 3H_2O$	$3.3 \times 10^{-4} \pm 15.8 \times 10^{-5}$
Cisplatin	$1.1 \times 10^{-5} \pm 4.9 \times 10^{-7}$

References

1. Guo, Q.; Li, L.; Dong, J.; Liu, H.; Xu, T.; Li, J. Synthesis, crystal structure and interaction of l-valine Schiff base divanadium(V) complex containing a V2O3 core with DNA and BSA. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2013**, *106*, 155–162, doi:10.1016/j.saa.2012.12.089.