Supporting Information (SI)

Three Peroxidovanadium(V) Compounds Mediated by Transition Metal Cations for Enhanced Anticancer Activity

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Table S1. Crystallographic Data for K[$VO(O_2)$(tricine)]·H_2O (**V1**), K[$VO(O_2)$(edda)]·H_2O (**V2**), and KO[$VO(O_2)$(aoida)] (**V3**)

Crystal	V1	V2	V3
Formula	$C_6H_{13}KNO_9V$	$C_6H_{12}KN_2O_8V$	$C_6H_8KN_2O_9V$
Formula weight	333.21	329.97	342.18
Crystal size [mm³]	0.13×0.12×0.11	0.13×0.12×0.11	0.20×0.20×0.10
Temperature [K]	293(2)	100(10)	293(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	P21/m	P21/c
a [Å]	15.149(4)	7.036(5)	21.717(4)
b [Å]	7.717(2)	5.877(5)	7.836(16)
c [Å]	18.928(7)	12.660(9)	15.792(3)
α [°]	90	90	90
β [°]	90	90.168(7)	108.90(3)
γ [°]	90	90	90
V [Å³]	2212.8(12)	523.52(7)	2542.5(10)
Z	8	2	4
μ [mm^{-1}]	1.316	1.423	1.150
***F* (000)**	1360	440	1380
T_{min}; T_{max}	0.843; 0.865	0.831; 0.855	0.803;0.894
Collected reflections	5657	9277	4677
R_{int}	0.1162	0.0635	0.0556
Obs. Reflections [$I \geq 2\sigma(I)$]	1941	1475	4677
No. refined parameters	164	139	343
wR_2 (all data)	0.1909	0.1987	0.2037
R_1 [$I \geq 2\sigma(I)$]	0.0801	0.0765	0.0753
GooF on F^2	1.032	1.200	1.068
CCDC	1855753	1855754	1855755

Table S2. Selected Bond Lengths (Å) and Angles (deg) for K[$VO(O_2)$(tricine)]·H_2O (**V1**), K[$VO(O_2)$(edda)]·H_2O (**V2**), and KO[$VO(O_2)$(aoida)] (**V3**)

	V1		**V2**		**V3**
V1-O6	1.886(5)	**V1-O6**	1.901(6)	**V1-O4**	1.843(5)
V1-O7	1.918(6)	**V1-O1**	1.919(5)	**V1-O5**	1.866(6)
O6-O7	1.437(8)	**O1-O6**	1.446(4)	**O4-O5**	1.417(3)
V1-O8	1.609(5)	**V1-O2**	1.605(4)	**V1-O1**	1.604(5)
O6-V1-O7	44.40(2)	**O1-V1-O6**	44.46(2)	**O4-V1-O5**	44.90(2)
V1-O6-O7	69.00(3)	**V1-O6-O1**	68.43(3)	**V1-O4-O5**	68.39(3)
V1-O7-O6	66.60(3)	**V1-O1-O6**	67.11(3)	**V1-O5-O4**	66.71(3)
O6-V1-O8	102.35(3)	**O1-V1-O2**	103.26(3)	**O1-V1-O4**	104.32(3)
O7-V1-O8	98.12(3)	**O2-V1-O6**	91.77(3)	**O1-V1-O5**	104.27(3)

Table S3. In vitro cytotoxicity compound **V1**-**V3** with or without the mediation of Mn^{2+} or Fe^{2+} toward MCF-7, A549 and BEAS-2B cells for 24h.

Compound	**Cytotoxicity in different cell lines (IC_{50} ± SD, μM)**			**SF[a]**
	MCF-7	**A549**	**BEAS-2B**	
V1	18.7 ± 0.92	16.5 ± 0.82	39.2 ± 2.9	2.10
V1+Mn^{2+}	5.22 ± 0.25	8.27 ± 0.42	30.3 ± 1.9	5.80
V1+Fe^{2+}	10.3 ± 0.53	11.3 ± 0.58	32.4 ± 2.0	3.14
V2	29.8 ± 1.8	34.6 ± 2.4	48.1 ± 4.0	1.61
V2+Mn^{2+}	14.1 ± 0.65	20.6 ± 1.1	33.7 ± 2.3	2.40
V2+Fe^{2+}	24.2 ± 1.2	34.2 ± 2.1	38.5 ± 3.5	1.60
V3	5.17 ± 0.27	12.9 ± 0.65	38.9 ± 3.6	7.52
V3+Mn^{2+}	2.23 ± 0.11	4.56 ± 0.23	30.2 ± 1.9	13.5
V3+Fe^{2+}	2.91 ± 0.15	4.72 ± 0.24	32.0 ± 2.0	11.0

[a] SF (Selectivity Factor) is defined as IC_{50} in BEAS-2B/IC_{50} in MCF-7.

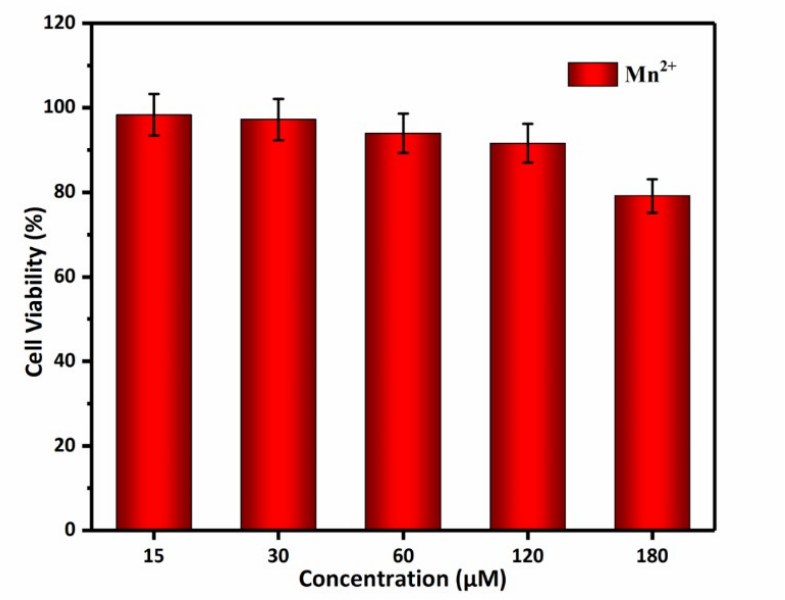

Fig. S1 Cell viabilities of MCF-7 cells at different Mn^{2+} concentrations for 24 h.

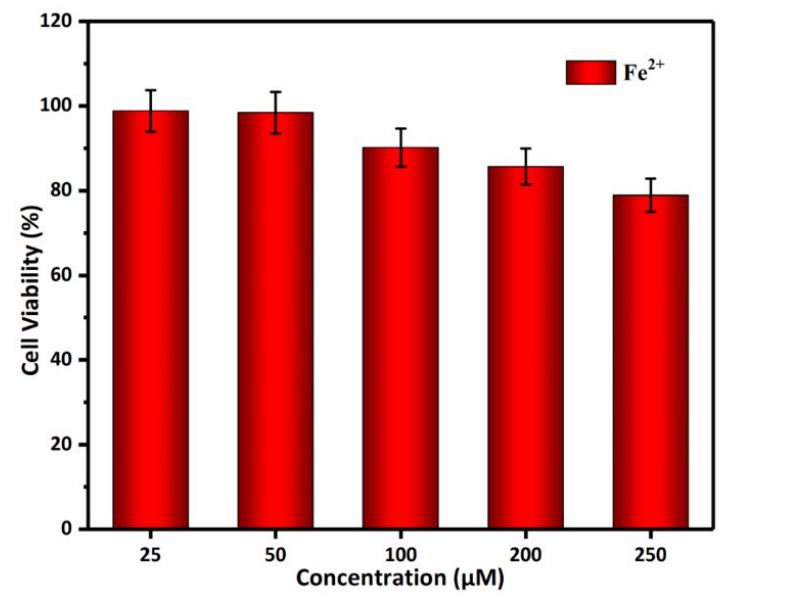

Fig. S2 Cell viabilities of MCF-7 cells at different Fe^{2+} concentrations for 24 h.

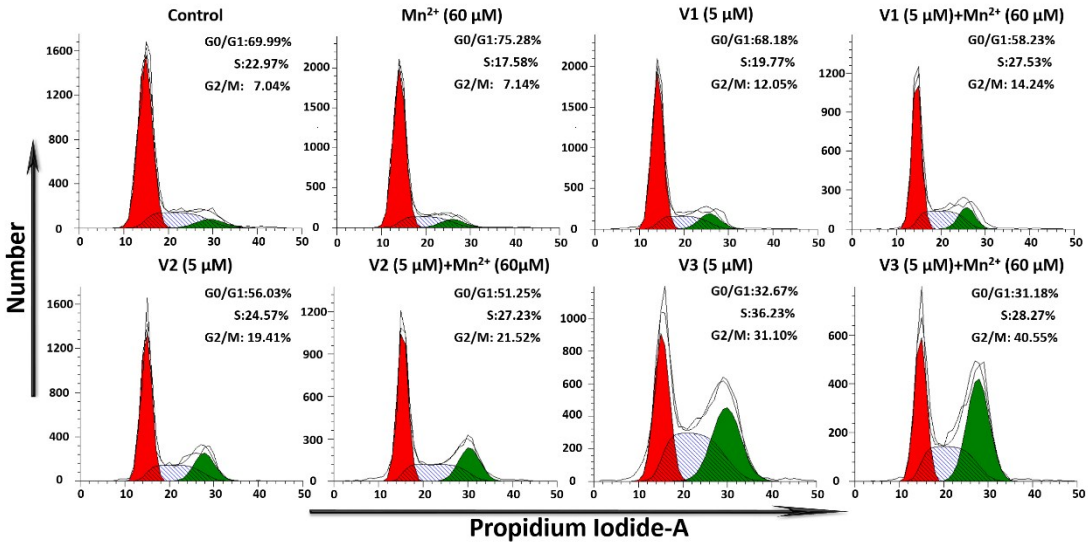

Fig. S3 Flow cytometry analysis for cell cycle distribution of MCF-7 cells induced by different reagents for 24 h. Cell staining: PI.

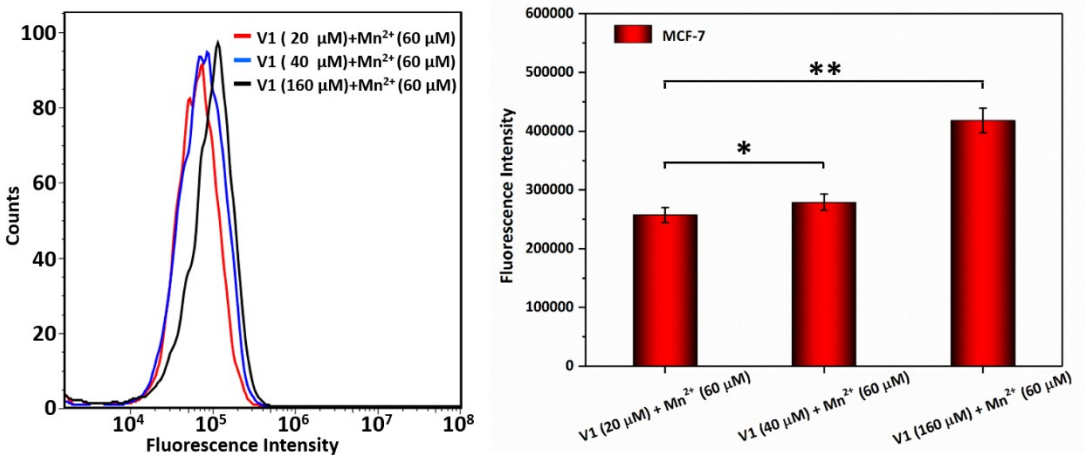

Fig. S4 Flow cytometry detection intracellular ROS levels by DCFH-DA staining after 4 h of co-incubation with Mn^{2+} and different concentrations of compounds **V1** for MCF-7 cells. (p values: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$)

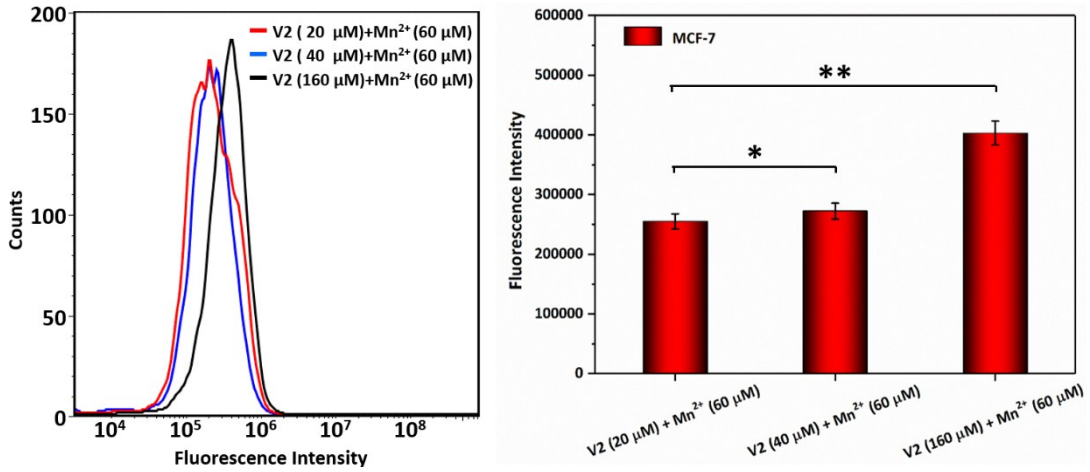

Fig. S5 Flow cytometry detection intracellular ROS levels by DCFH-DA staining after 4 h of co-incubation with Mn^{2+} and different concentrations of compound **V2** for MCF-7 cells. (p values: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$)

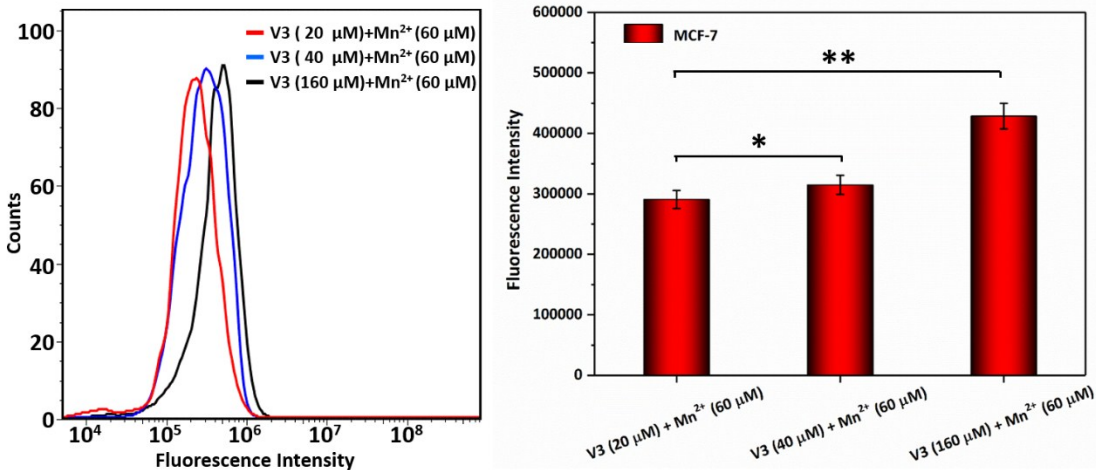

Fig. S6 Flow cytometry detection intracellular ROS levels by DCFH-DA staining after 4 h of co-incubation with Mn^{2+} and different concentrations of compound **V3** for MCF-7 cells. (p values: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$)

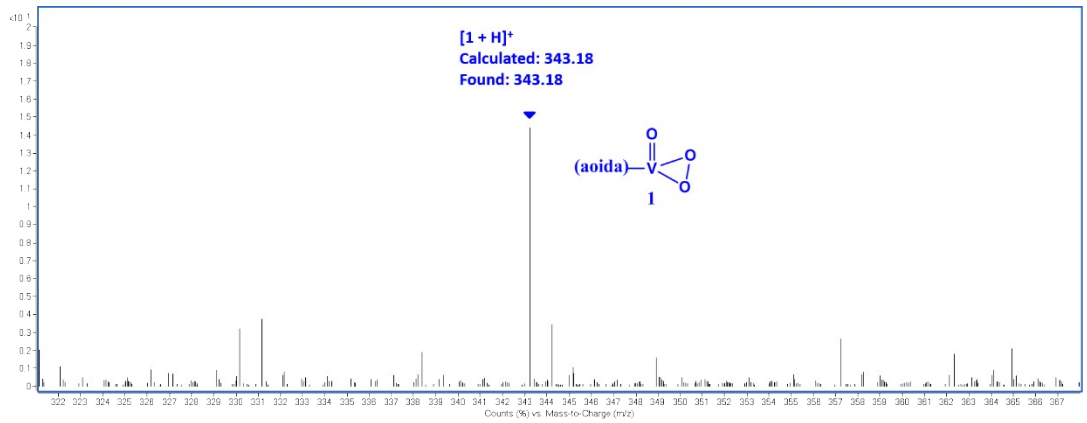

Fig. S7 LC-MS spectra of compound **V3** (**1**).

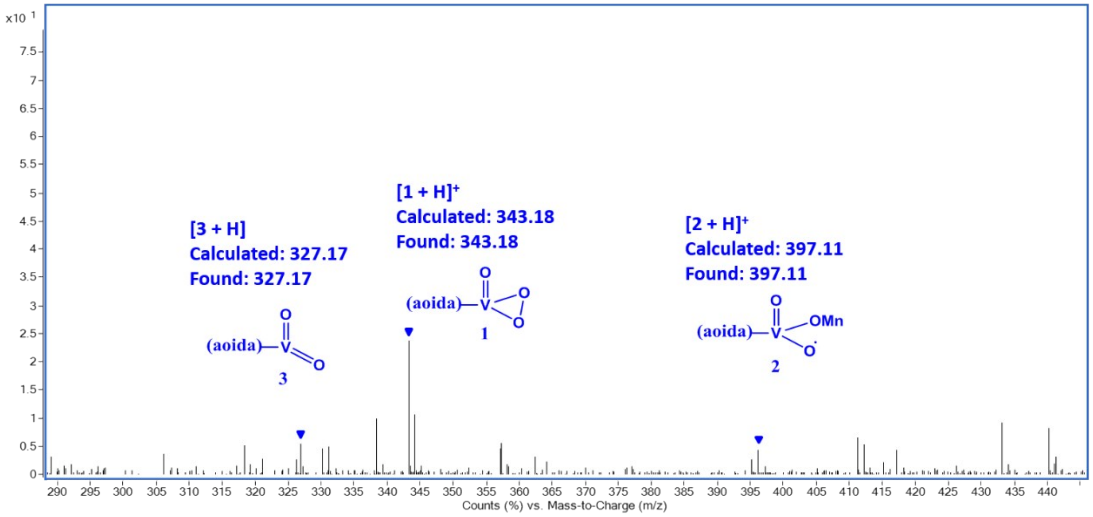

Fig. S8 LC-MS spectra of compound **V3** (**1**) mediated by Mn^{2+}.

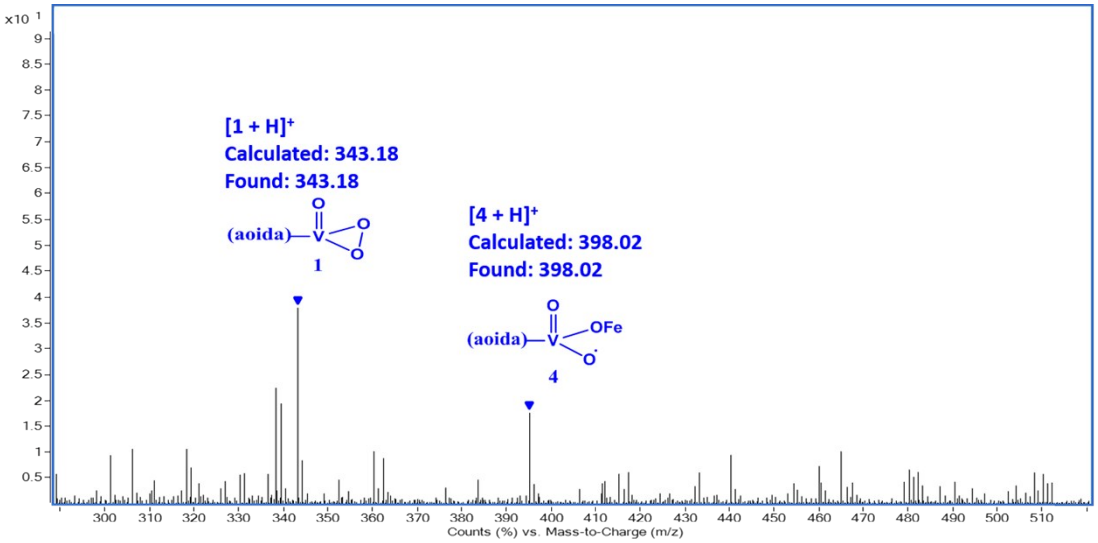

Fig. S9 LC-MS spectra of compound **V3** (**1**) mediated by Fe^{2+}.