Electronic Supplementary Material (ESI) for Dalton Transactions
This journal is © The Royal Society of Chemistry 2014

Supporting information for

Interaction of oxovanadium(IV)–salphen complexes with bovine serum albumin and their cytotoxicity against cancer

Velusamy Gomathi Sankareswari[a], Devaraj Vinod[b], Ayyasamy Mahalakshmi[c], Meena Alamelu[d] Ganesan Kumaresan[d], Ramasamy Ramaraj[a]* and Seenivasan Rajagopal[a]*

Table S1. ^{1}HNMR data of the salophen ligands

Ligand	δ OH	δ Ar-H	δ N=CH	δ CH_3	δ OCH_3
1	13.10(s,2H)	6.90-7.40(m,12H)	8.64(s,2H)	_	_
2	13.10(s,2H)	6.92-7.50(m,10H)	8.58(s,2H)	_	_
3	13.15(s,2H)	6.81-7.51(m,10H)	8.57(s,2H)	_	_
4	13.10(s,2H)	6.99-7.40(m,10H)	8.57(s,2H)	_	_
5	12.81(s,2H)	6.93-7.33(m,10H)	8.58(s,2H)	2.30(s,6H)	_
6	12.60(s,2H)	6.89-7.31(m,10H)	8.60(s,2H)	_	3.80(s,6H)
7	13.50(s,2H)	7.00-7.91(m,8H)	8.92(s,2H)	_	_
8	13.54(s,2H)	7.21-7.43(m,8H)	8.66(s,2H)	1.32(s,18H),1.43(s,18H)	_

This journal is © The Royal Society of Chemistry 2014

Table S2. ^{13}C NMR data of ligands

Ligand	^{13}C NMR
1	117.5,118.9,119.2,119.7,127.6,132.3,142.5,161.3,163.7
2	119.1,119.6,119.9,123.6,128.2,131.2,133.2,142.1,159.8,162.4
3	110.5,119.6,120.6,128.2,134.3,136.1,142.2,160.4,162.4
4	20.3,117.3,118.8,119.7,127.5,128.0,132.2,134.3,142.7,159.1,163.7
5	30.9,56.0,115.3,118.4,119.7,120.8,127.7,142.6,152.2,155.6,163.4
6	29.4,31.4,34.1,35.1,118.3,119.8,126.7,127.2,128.1,137.1,140.3,142.7,158.5,164.7

Table S3. EPR data for oxovanadium(IV)-salophen complexes

Complex	g_{iso}	g_{II}	$g_{\perp}$	A_{II} cm^{-1}	A_{iso} cm^{-1}
I	1.960	1.976	1.286	$304.5x10^{-4}$	$198.0x10^{-4}$
II	1.960	1.950	1.319	$292.6x10^{-4}$	$195.0x10^{-4}$
VI	1.960	1.977	1.284	$303.2x10^{-4}$	$196.9x10^{-4}$
VIII	1.960	1.950	1.319	$292.6x10^{-4}$	$197.8x10^{-4}$

This journal is © The Royal Society of Chemistry 2014

Table S4. IR data of the salophen ligands

Ligand	ν(C-OH)	ν(C=N)	ν(C-N)
1	3054	1614	1344
2	3077	1612	1313
3	3073	1612	1313
4	3085	1617	1297
5	3300	1618	1298
6	3313	1614	1280
7	3058	1614	1294
8	3056	1614	1319

Table S5. IR data of the oxovanadium (IV)-salophen complexes

Complex	ν(C=N)	ν(C-N)	ν(C-O)	ν(V=O)	ν(V-N)	ν(V-O)
I	1607	1315	1196	978	542	484
II	1607	1310	1280	970	522	495
III	1605	1306	1246	968	515	443
IV	1618	1340	1298	978	532	419
V	1620	1298	1263	978	536	469
VI	1595	1285	1220	974	540	491
VII	1603	1325	1227	987	540	487
VIII	1601	1313	1250	976	542	484

This journal is © The Royal Society of Chemistry 2014

Table S6. Excited-state dynamic (K_D) and static (K_S) Stern–Volmer constant and quenching rate constants (k_q) of BSA with salphen ligands and oxovanadium(IV)–salphen complexes.

Ligand 1	6.4×10^5	1.9×10^3	1.1×10^{13}
Ligand 7	2.0×10^4	3.2×10^5	3.4×10^{12}
Complex II	4.9×10^4	1.0×10^4	8.3×10^{12}
Complex IV	5.1×10^4	1.2×10^4	8.7×10^{12}
Complex V	1.1×10^5	1.3×10^4	1.8×10^{13}
Complex VI	1.0×10^5	3.3×10^4	1.7×10^{13}
Complex VII	1.6×10^5	2.2×10^4	2.7×10^{13}
Complex VIII	6.0×10^4	1.6×10^4	1.0×10^{13}

Table S7. Förster Energy Transfer Parameters (FRET) parameters of salphen ligands and oxovanadium(IV)–salphen complexes with BSA.

Sample	J (M^{-1} cm^3)	R_0 (nm)	r (nm)	E
Ligand **1**	1.8×10^{-14}	2.72	2.09	0.72
Ligand **2**	$1.8 \times 10\text{-}^{14}$	2.73	2.75	0.41
Ligand **3**	1.3×10^{-14}	2.61	2.49	0.52
Ligand **4**	3.2×10^{-14}	3.03	3.21	0.38
Ligand **5**	2.0×10^{-14}	2.83	2.78	0.51
Ligand **6**	1.7×10^{-14}	2.74	2.28	0.63
Ligand **7**	7.0×10^{-15}	2.32	2.30	0.50

This journal is © The Royal Society of Chemistry 2014

Complex **I**	2.3×10^{-14}	2.94	2.23	0.69
Complex **III**	2.1×10^{-14}	2.80	2.88	0.34
Complex **V**	4.0×10^{-14}	3.12	2.98	0.61
Complex **VI**	3.5×10^{-14}	3.04	1.39	0.76
Complex **VII**	2.3×10^{-14}	2.82	3.49	0.57

Table S8. Circular Dichroism spectral data of BSA with oxovanadium(IV)–salphen complexes.

	μM	**λ max**	**M deg**	**α– helicity (%)**
BSA alone		208	–122.94	59
		222	–112.69	53
Complex				
I	1	208	–99.50	45
	2	208	–71.14	28
II	1	208	–90.22	40
	2	208	–39.84	10
III	1	208	–88.75	38
	2	208	–67.75	26
IV	1	208	–89.71	39
	2	208	–69.16	27
V	1	208	–77.48	32
	2	208	–70.63	28
VI	1	208	–93.16	41
	2	208	–70.18	28
VII	1	208	–106.37	49
	2	208	–69.69	27
VIII	1	208	–94.13	42
	2	208	–69.67	27

This journal is © The Royal Society of Chemistry 2014

Table S9 The IC50 values for V(IV) complexes against AGS gastric cell lines.

Complex	IC_{50} values (µM)
I	1.2
II	0.4
III	38.7
IV	53.7
V	36.6
VI	0.8
VII	33.2
VIII	38.9

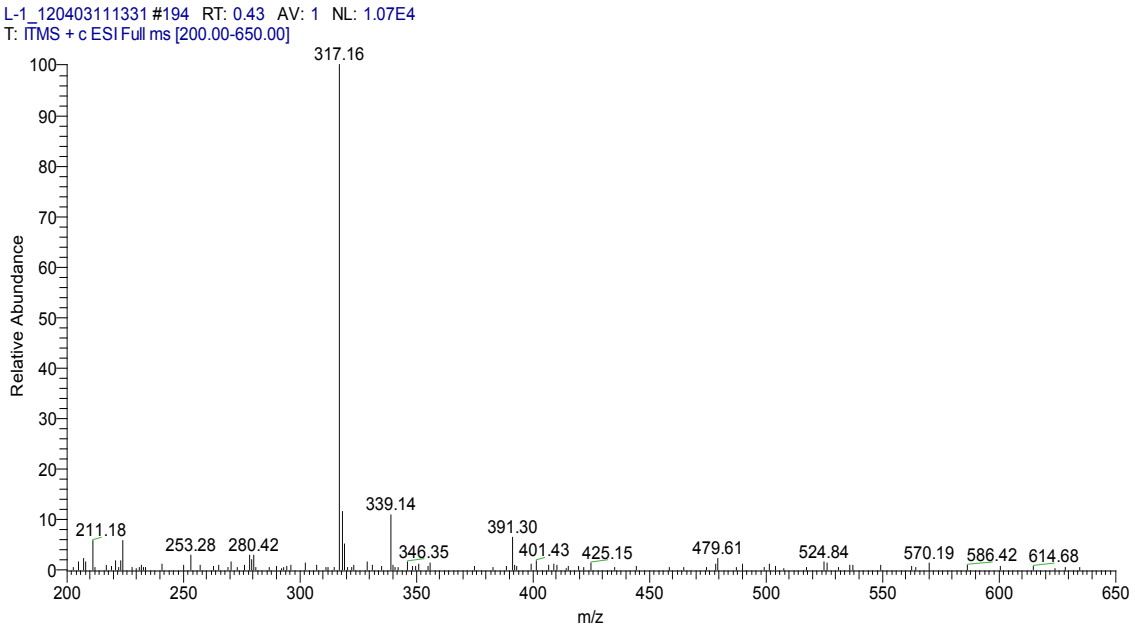


Fig. S1. ESI-MS spectrum of Ligand **1.**

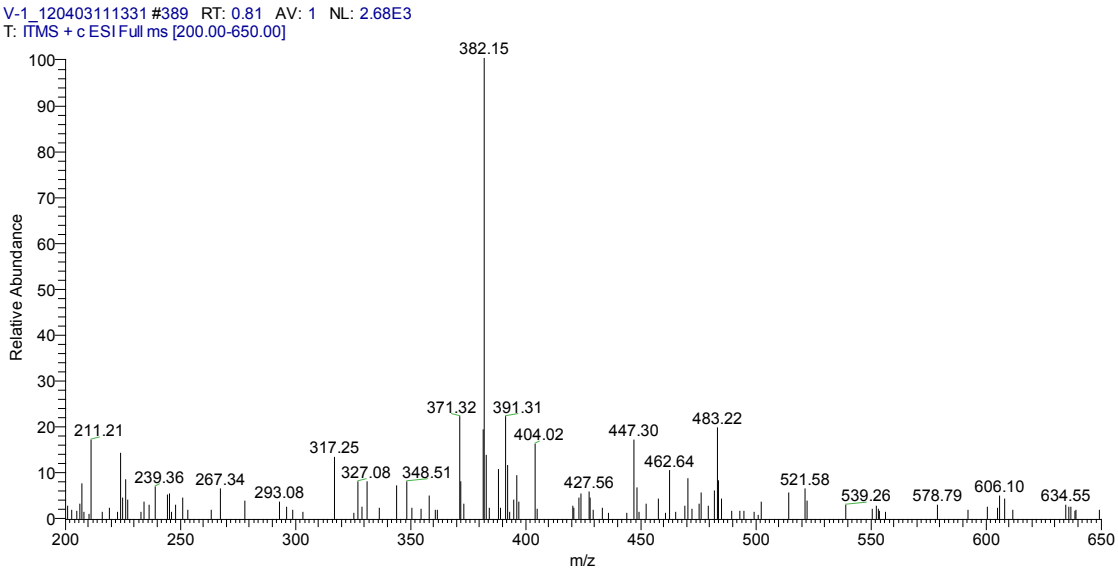
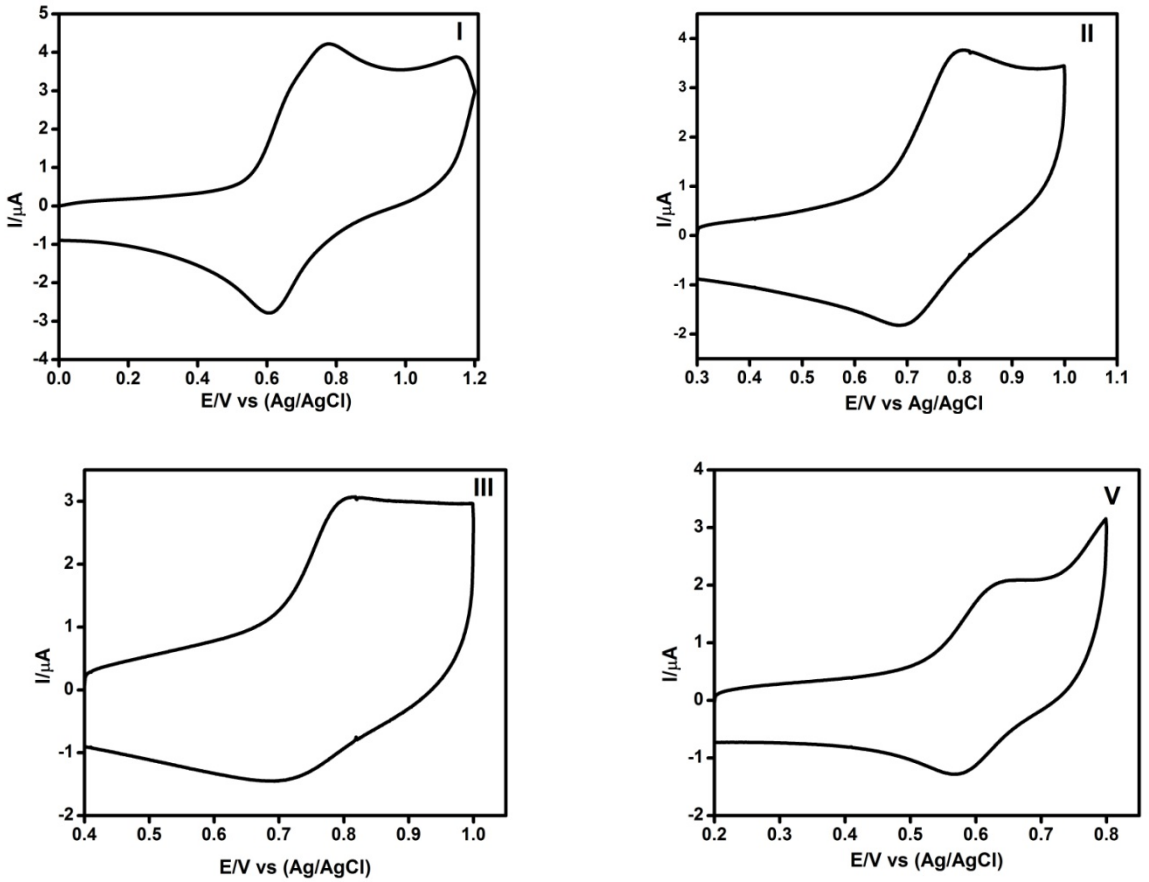


Fig. S2. ESI-MS spectrum of Complex **I.**



This journal is © The Royal Society of Chemistry 2014

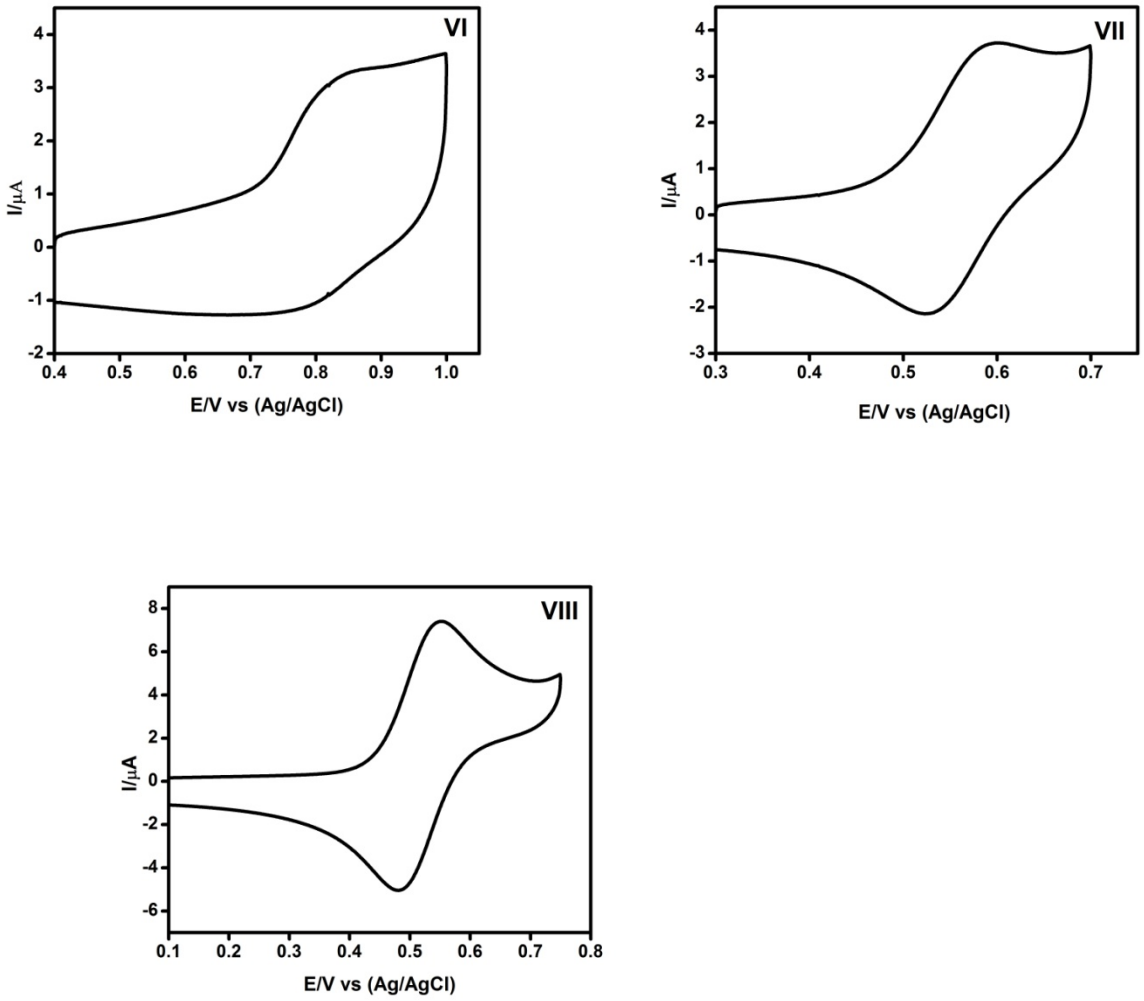


Fig.S3. Cyclic voltammograms of complexes **I, II, III, V, VI, VII** and **VIII** at room temperature in CH_3CN with 0.1 M tetrabutylammonium per chlorate as the supporting electrolyte, glassy carbon, platinum wire and Ag/AgCl as working, supporting and reference electrodes respectively, under nitrogen. Scan speed : 100 mV s^{-1}.

This journal is © The Royal Society of Chemistry 2014

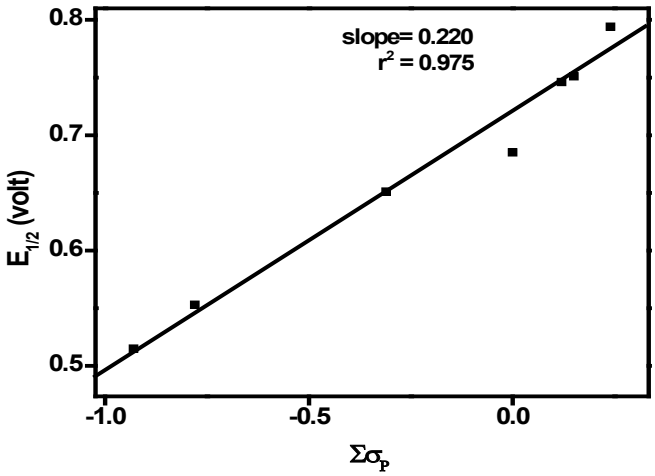


Fig. S4. Hammett plot

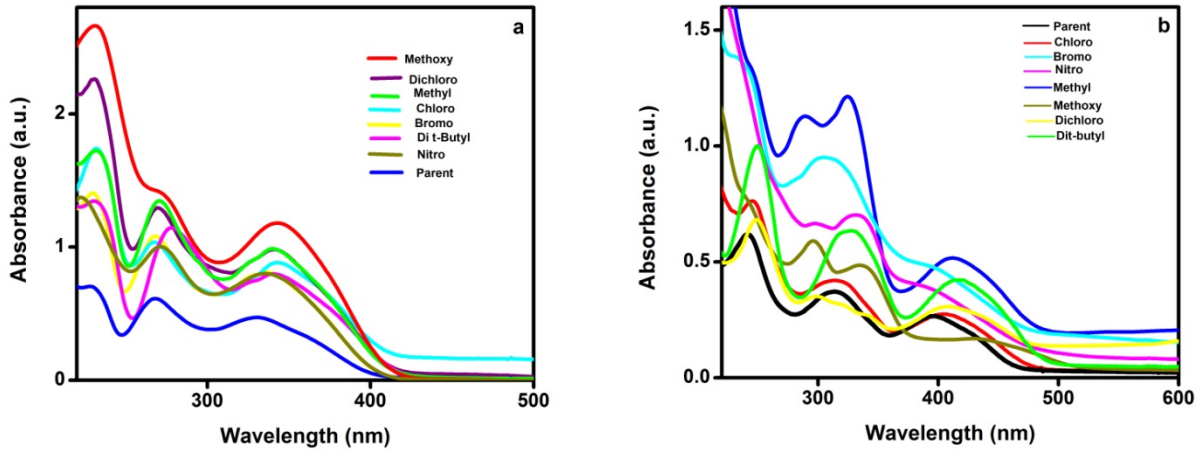
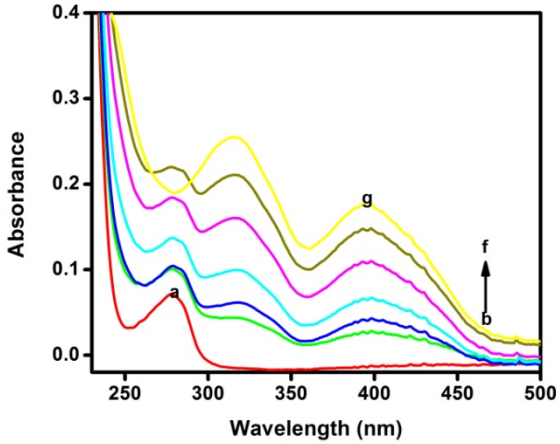


Fig. S5. UV-visible overlay spectra of a) ligands b) complexes.



This journal is © The Royal Society of Chemistry 2014

Fig. S6 Absorption spectral changes of BSA (2μM) with the addition of complex **I** (0–20μM) in 2%CH_3CN–98%H_2O (v/v), pH=7.4 at 300 K.

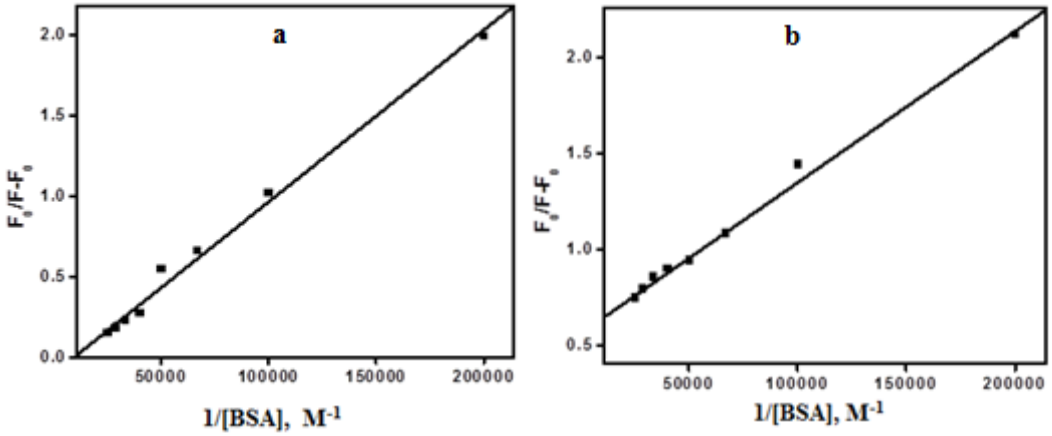


Fig. S7 Modified Benesi-Hildebrand plot of a)Ligand **1** b) Complex **I** with BSA.

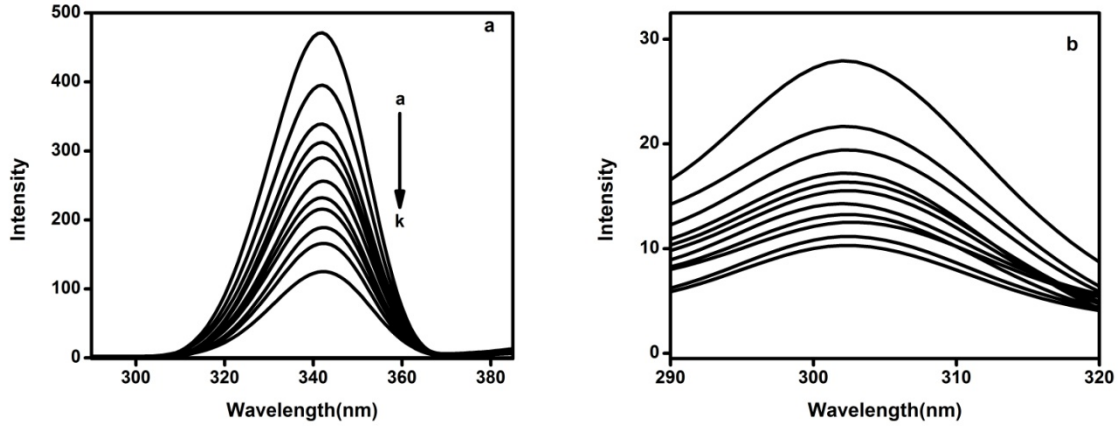


Fig. S8 Synchronous fluorescence spectra of BSA (5 μM) upon addition of complex **I** (0-50 μM.) a) Δλ = 60 nm b) Δλ = 15nm 2%CH_3CN–98%H_2O (v/v), pH=7.4 at 300 K.

This journal is © The Royal Society of Chemistry 2014

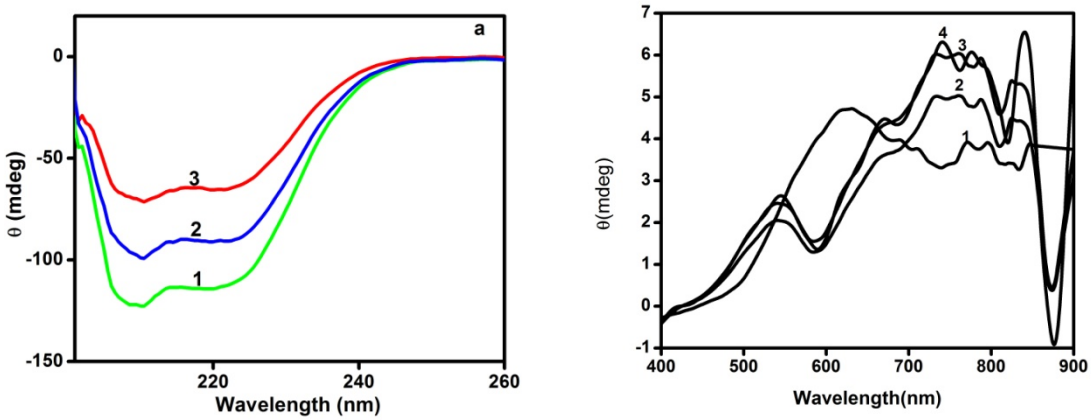


Fig . S9 CD Spectra of BSA (2×10^{-6} M)a) In the UV region in the absence (1) and in the presence of a) complex **I** with concentration (2) and (3) b) In the visible region complex **I** at 1×10^{-6} M (2) , 2×10^{-6} M (3) 3×10^{-6} M (4) at pH 7.4 and 37° C.

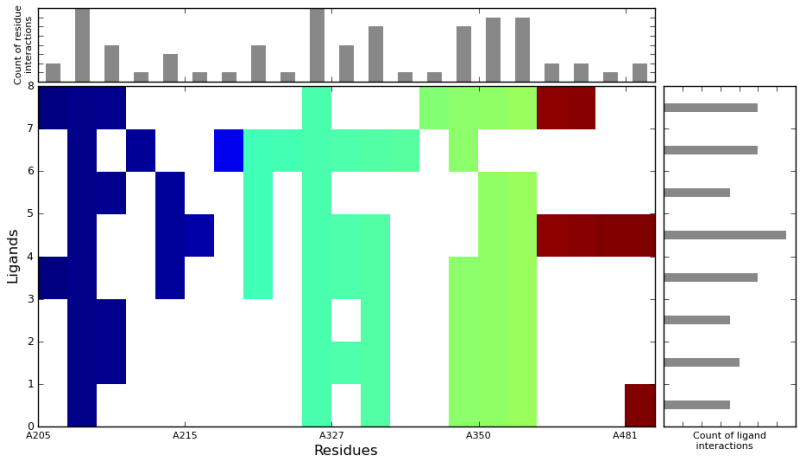


Fig. S10 The plot shows the overall interaction of our synthesized compounds (y axis) with different amino acid residues (x axis) with respective interaction count / influence of synthesized ligand against amino acid or vice versa as shown in right side of the plot (y axis :count of ligand interactions) and above the plot (x axis :count of residue interactions).

This journal is © The Royal Society of Chemistry 2014

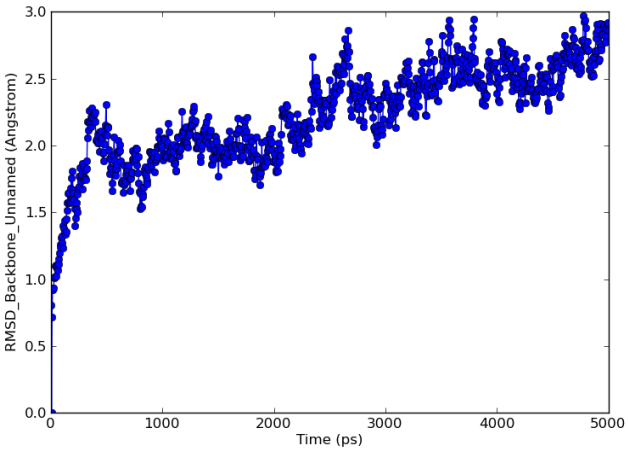


Fig.S11 RMSD of the protein backbone against the time scale of 5 ns explcit molecular dynamics simulation.

Latest.mpeg

Fig.S12 Video clip file for the explicit molecular dynamics of the complex **V** with BSA.

This journal is © The Royal Society of Chemistry 2014

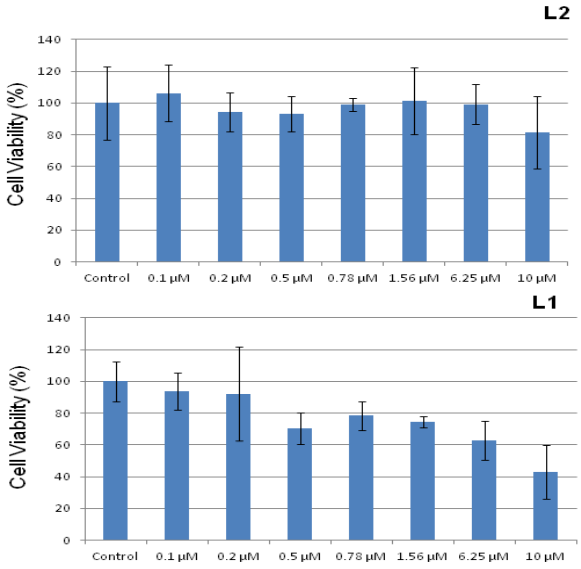


Fig.S13 Cell viability of salphen ligands **1and 8** on AGS gastric cell line *in vitro*.

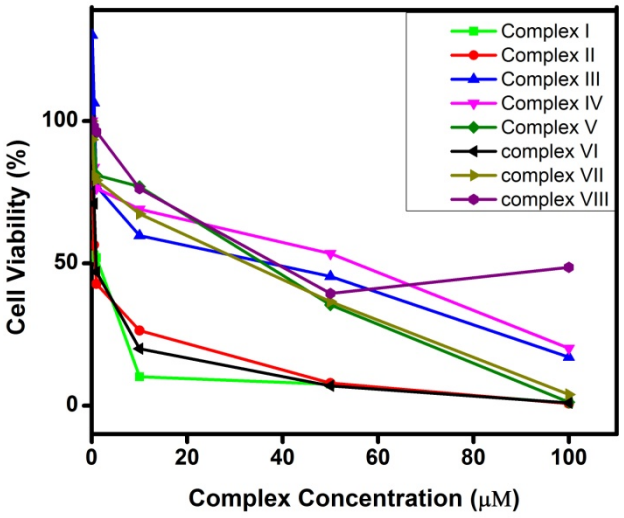


Fig.S14 Cytotoxic activity of oxovanadium (IV) complexes against AGS gastric cell lines.