Electronic supplementary Information

Polystyrene bound oxidovanadium(IV) and dioxidovanadium(V) complexes of histamine derived ligand for the oxidation of methyl phenyl sulfide, diphenyl sulfide and benzoin

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Electronic spectral study

The electronic spectral studies of Hsal–his and [V^{IV}O(sal–his)(acac)] have been described earlier in detail.[21] The electronic spectra of anchored and neat complexes are reproduced in Figs. S1 and S2, respectively. The electronic spectral patterns exhibited by the polymer-bound ligand and metal complexes are similar (Table S1) to those obtained for the corresponding non-polymer bound analogues, except for the low intensity of bands. The lower energy (less intense) bands appearing at 532 and 776 nm due to d – d transitions in [V^{IV}O(sal–his)(acac)] could not be located in the polymer-bound complex due to its poor loading in the polymer matrix. A band appearing at 394 nm in [V^{V}O$_2$(sal–his)] is assigned to a ligand-to-metal charge transfer (lmct) transition. Only a weak shoulder band could be observed in the polymer-bound dioxidovandium(V) complex in this region.

Table S1 Electronic spectral data of ligands and complexes

Compounds	Solvent	λ_{max} / nm
Hsal–his **I**	Methanol	214, 254, 314, 402
[V^{IV}O(acac)(sal–his)] **3**	Methanol	215, 257, 277, 319, 384, 532, 776
[V^{V}O$_2$(sal–his)] **4**	Methanol	213, 253, 279, 322, 394
PS-Hsal–his **II**	Nujol	211, 229, 286, 330, 414
PS–[V^{IV}O(acac)(sal–his)] **1**	Nujol	209, 280, 329, 416
PS–[V^{V}O$_2$(sal–his)] **2**	Nujol	206, 276, 340, 390

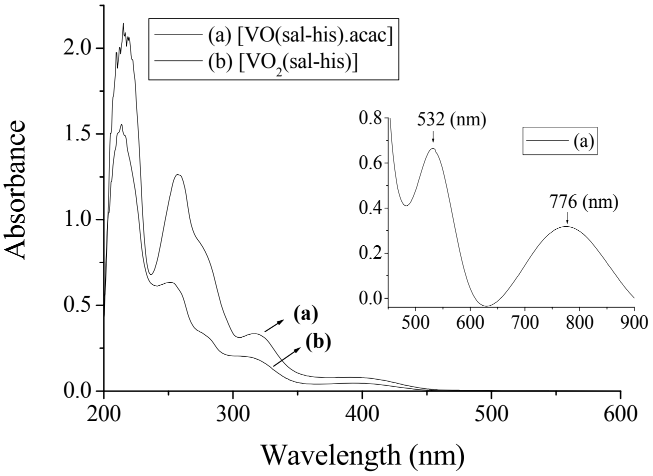

Fig. S1 Electronic spectra of neat metal complexes **3** and **4** in MeOH solution (ca. 10^{-4} M). The insert shows the spectrum of **1** in the visible range, recorded with a higher concentration of complex (ca. 10^{-3} M).

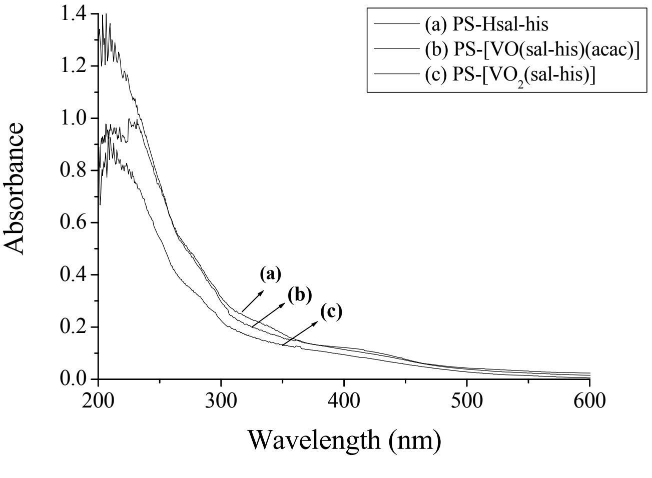

Fig. S2 Electronic spectra of polymer-anchored ligand and metal complexes dispersed in nujol mulls.

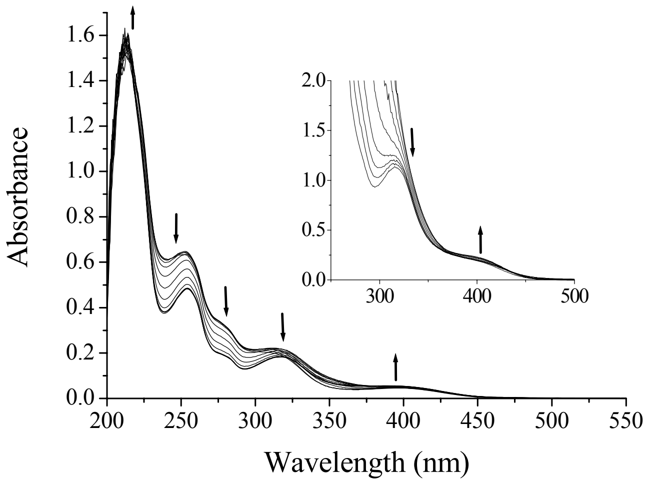

Fig. S3 Spectral changes observed during titration of [V^VO_2(sal–his)] **4** with H_2O_2. The spectra were recorded after successive additions of one drop portions of H_2O_2 (6.6×10^{-4} mmol of 30% H_2O_2 dissolved in 10 mL of methanol) to 50 mL of ca. 10^{-4} M solution of **4** in methanol. The inset shows the equivalent titration, but with higher concentration of [V^VO_2(sal–his)] (ca. 10^{-3} M) with one drop portions of H_2O_2 (2 mmol of 30% H_2O_2 dissolved in 5 mL of methanol).

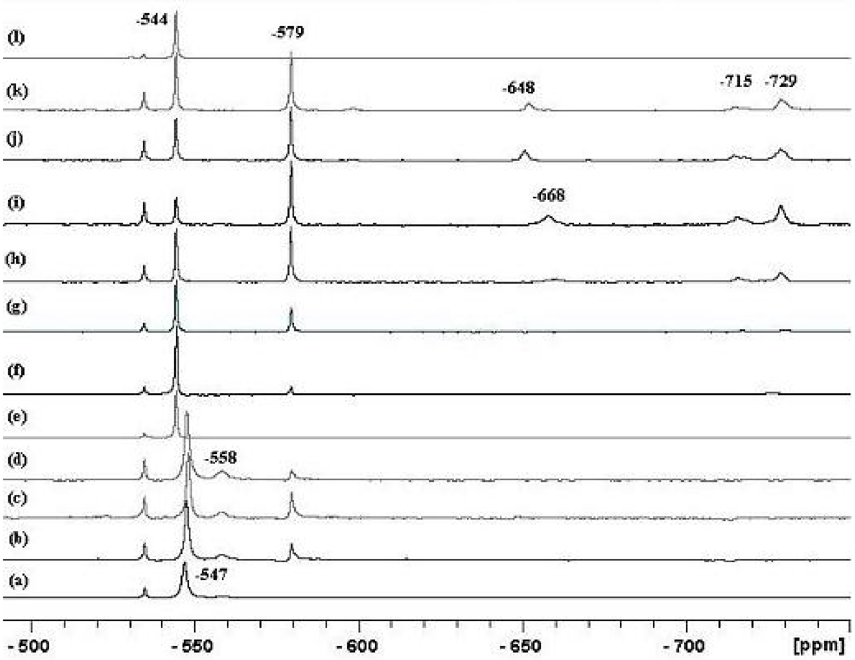

Fig. S4 ^{51}V NMR spectra for [V^{V}O$_2$(sal–his)] **4**: (a) in MeOH; (b) 0.5 eq. H_2O_2; (c) 1.0 eq. H_2O_2; (d) 1.5 eq. H_2O_2; (e) after 20 hr; (f) 0.5 eq. H_2O_2; (g) 1.0 eq. H_2O_2; (h) 1.5 eq. H_2O_2; (i) 2.0 eq. H_2O_2; (j) 1.0 eq. methyl phenyl sulfide; (k) 2.0 eq. methyl phenyl sulfide; (l) 2.0 eq. methyl phenyl sulfide (after 24 hr). All spectra were recorded including an external reference of aqueous vanadate at pH ~12 (peak at ca. –536 ppm).

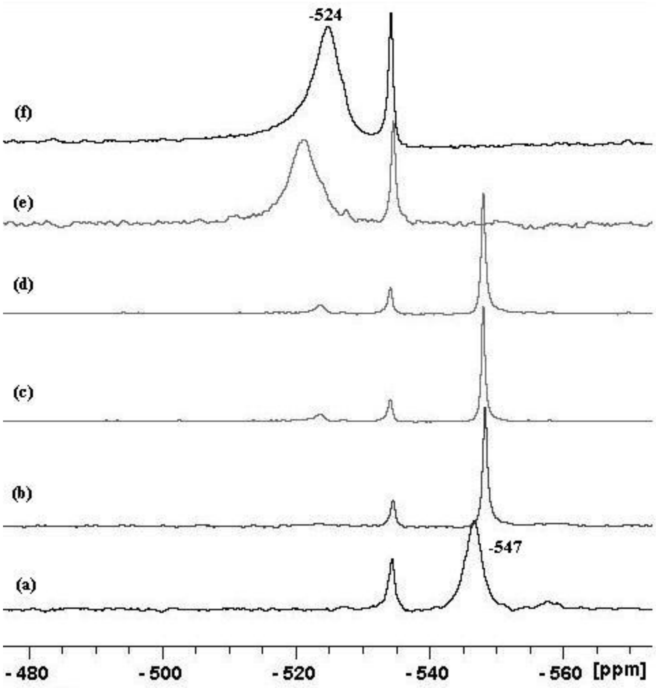

Fig. S5 ^{51}V NMR spectra for [V^{V}O$_2$(sal–his)]: (a) in MeOH, (b) 0.5 equiv HCl; (c) 1.0 equiv HCl; (d) 1.5 equiv HCl; (e) 2.0 equiv HCl; (f) 2.5 equiv HCl. All spectra were recorded including an external reference of aqueous vanadate at pH ~12 (peak at ca. –536 ppm).