

Supplementary Information

Vanadium (V) complexes of a tripodal ligand, their characterisation and biological implications

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Table S1. ^1H NMR spectral data

Compound	–OH	–NH	– <i>tert</i> -butyl	–NCH ₂ CH ₂ –	–CH ₂ N–	Aromatic
H ₂ L ¹ 1	9.648(s, 2H)		1.377(s, 18H), 1.399(s, 18H)	2.913(s, 2H), 3.217(s, 2H)	4.850(s, 4H)	8.795(Py, s, 1H), 7.677(d, 1H), 7.648-7.662(m, 4H), 7.319-7.26 (m, 1H), 7.172-9.989(m, 2H)
[V ^{VO} (acac)(L ¹)] 1			1.31(s, 18H) 1.57(s, 18H)	2-2.05(d, 2H), 2.25(s, 2H)	3.44- 3.41(d, 2H) 2.92(s, 2H)	8.44-8.42 (d, 1H Py), 7.51-7.47(m, 1H), 7.31-7.30(d, 2H), 7.06-7.05(m, 3H), 6.87-6.85(d, 1H)
[{V ^{VO} (L ¹)} ₂ μ–O] 3			0.86(s, 36H), 1.24(s, 36H)	2.80(s, 4H), 2.51(s, 4H)	6.03-6.00(d, 4H) 3.24-3.21(d, 4H)	9.83 (s, 2H Py), 7.36-7.33 (t, 2H), 7.02-6.99(t, 2H), 6.96(s 4H), 6.86(s, 4H) 6.70-6.68(d, 2H)
[{V ^{VO} (L ²)} ₂ μ–(OH) ₂] 5		4.20 (br s, 1H), 4.13 (br s, 1 H)	1.41-1.42(d, 36 H), 1.28-1.31(d, 36H)		4.01-3.98(d, 3H), 3.47-3.42(t, 3H), 3.23(s, 1H), 3.06(s, 1H)	7.31(s, 1H), 7.27(s, 2H), 7.05(s, 4H), 7.00(s, 1H)
[{V ^{VO} (L ²)} ₂ μ–O] 6		4.58 (br s, 1H), 4.19 (br s, 1 H)	1.41-1.43(d, 36H), 1.31-1.32(d, 36H)		4.00-3.98 (d, 4 H), 3.47-3.42 (m, 2 H), 3.21(s, 1H) 2.97 (s, 1H)	7.28 (s, 4H), 7.05(s, 2H), 7.00(s, 2H)

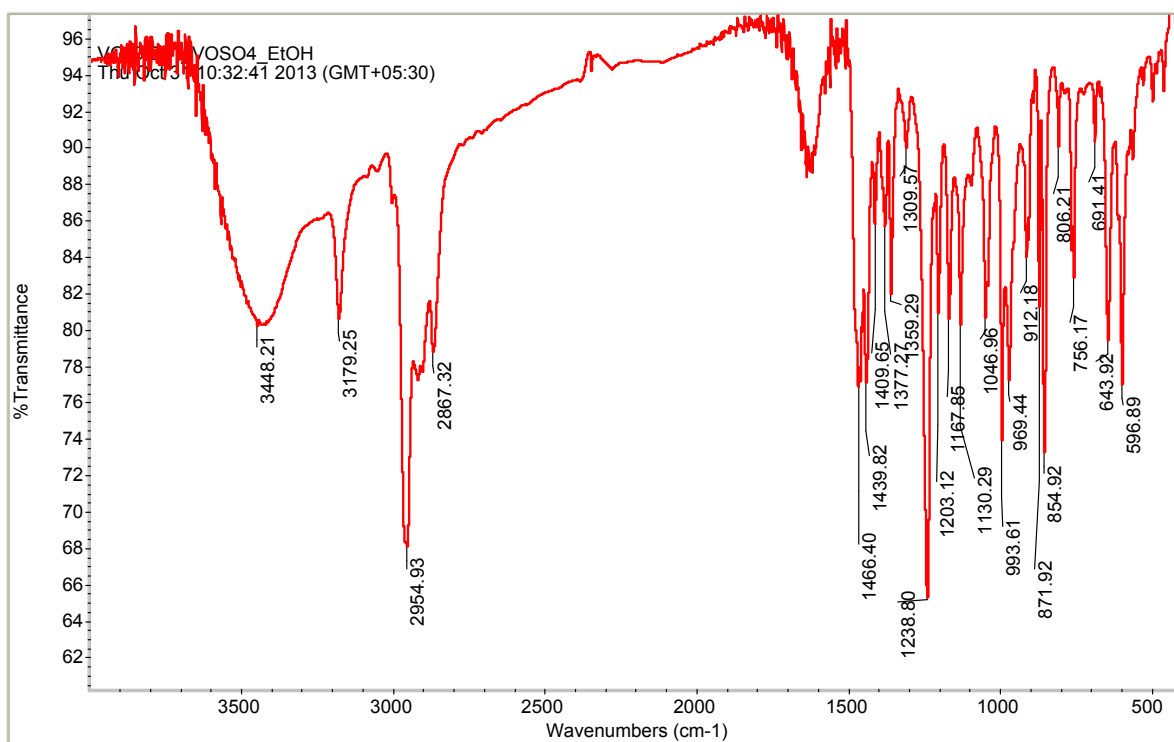


Fig. S1 IR Spectrum of the compound formulated as $\text{H}[\text{VVO}_2(\text{L}^2)]$ **4**

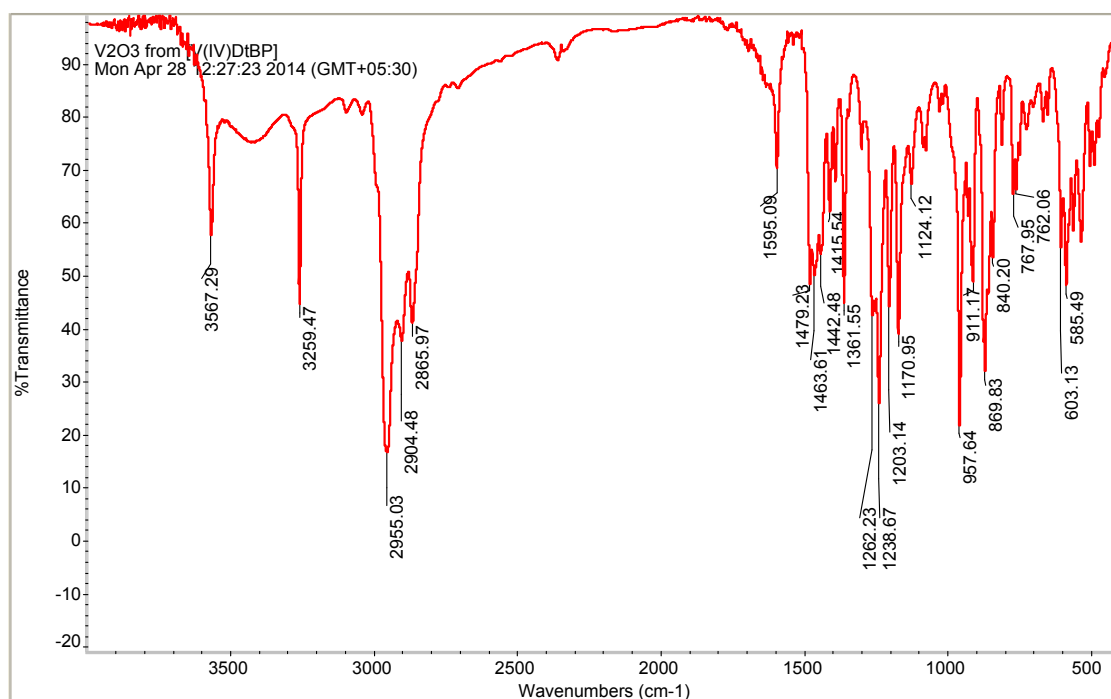


Fig. S2 IR Spectrum of $[\{\text{VVO}(\text{L}^2)\}_2\mu(\text{OH})_2]$ **5**

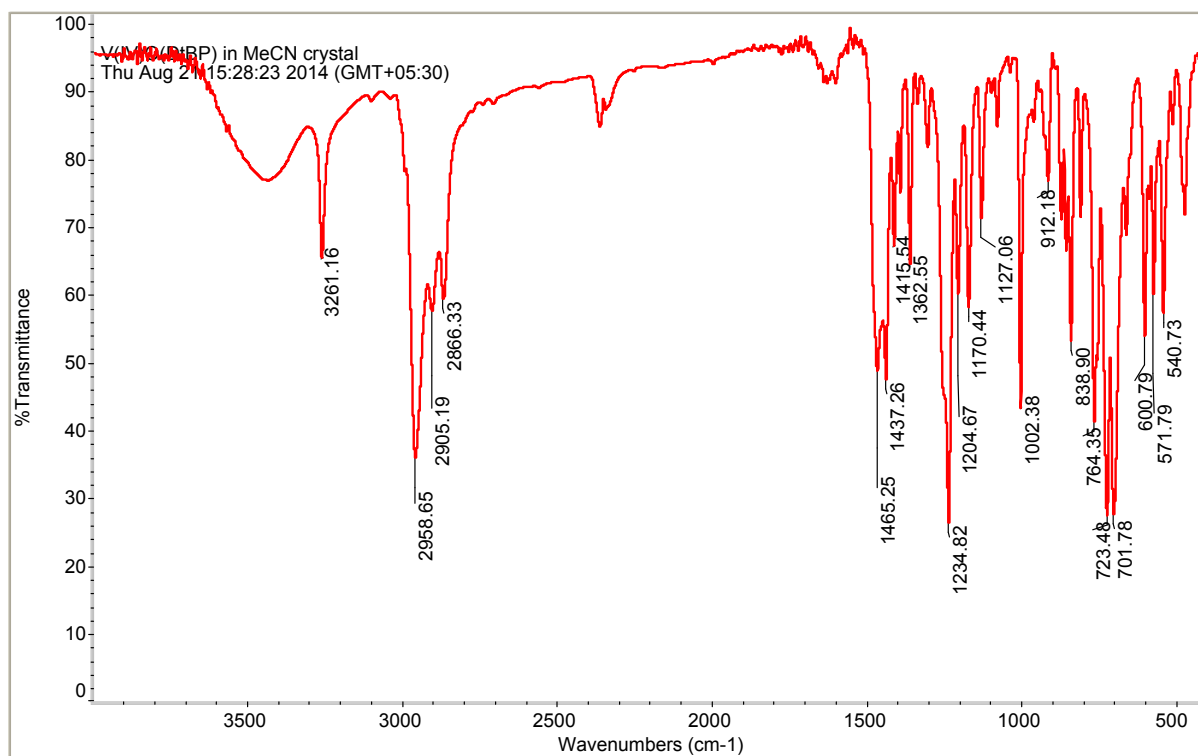


Fig. S3 IR Spectrum of $[\{V^VO(L^2)\}_2\mu-O]$ **6**

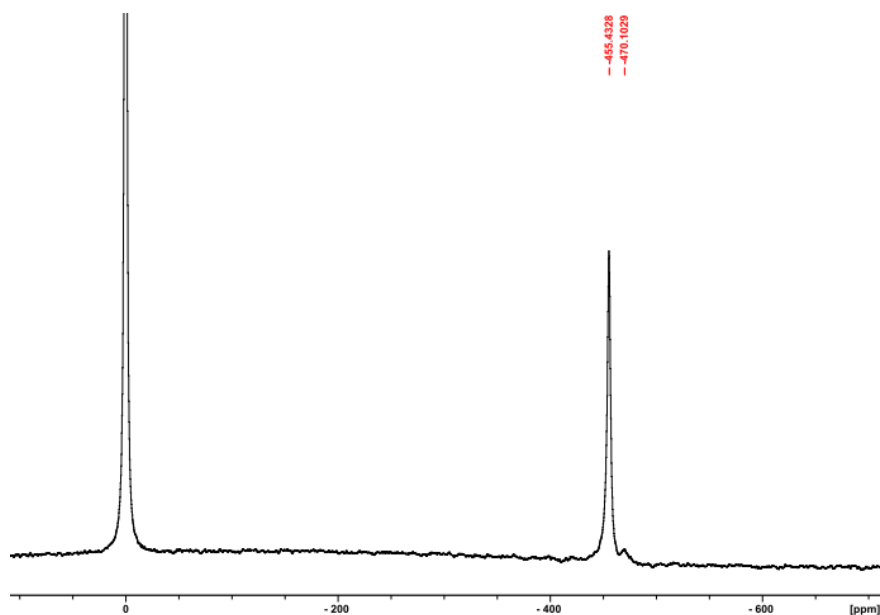


Fig. S4 ^{51}V NMR spectrum of **1** in CD_2Cl_2 . The peak at $\delta = 0$ ppm corresponds to external neat V^VOCl_3 .

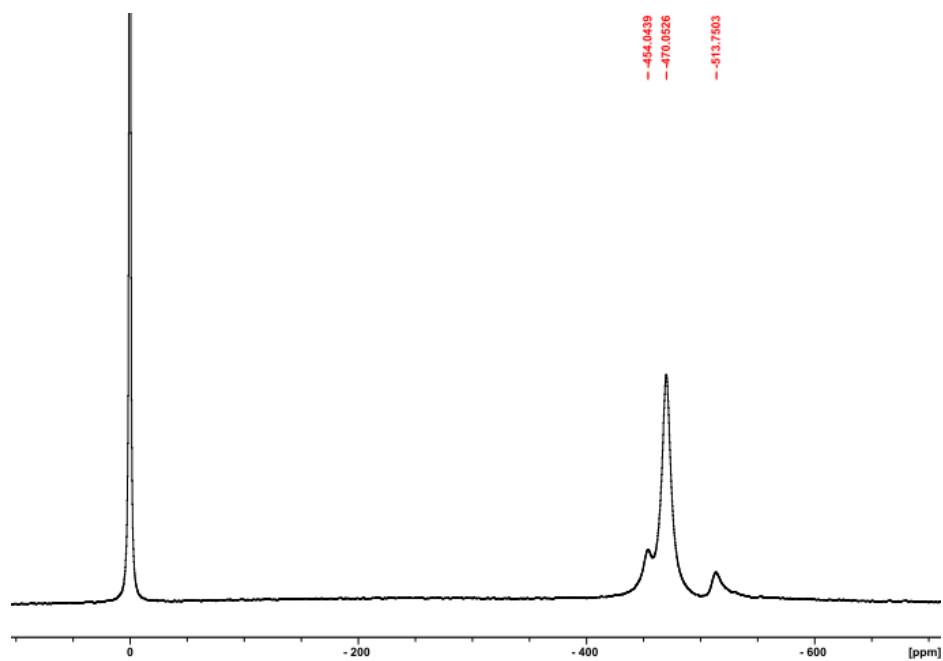


Fig. S5 ^{51}V NMR spectrum of **3** in CD_2Cl_2 . The peak at $\delta = 0$ ppm corresponds to external neat $\text{V}^{\text{VO}}\text{Cl}_3$.

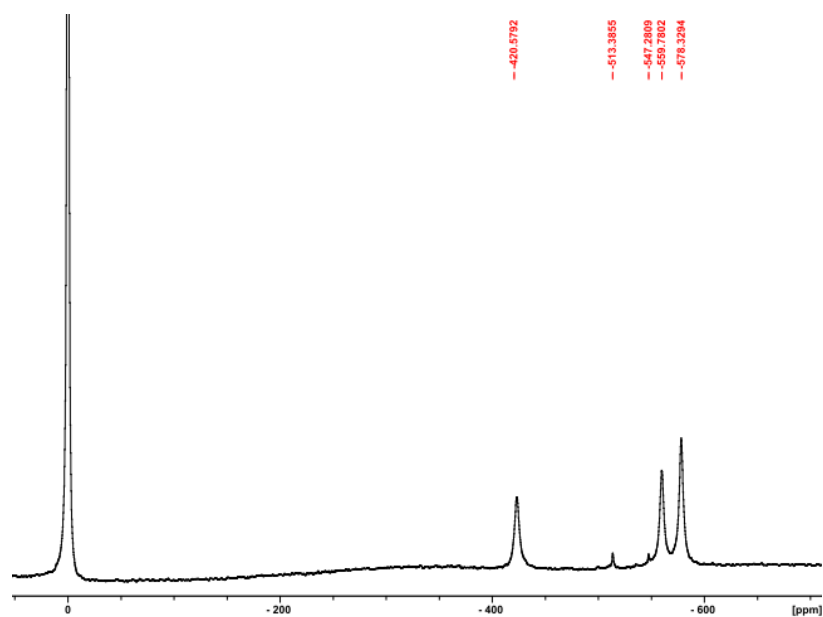


Fig. S6 ^{51}V NMR spectrum of **6** in CD_2Cl_2 . The peak at $\delta = 0$ ppm corresponds to external neat $\text{V}^{\text{VO}}\text{Cl}_3$.

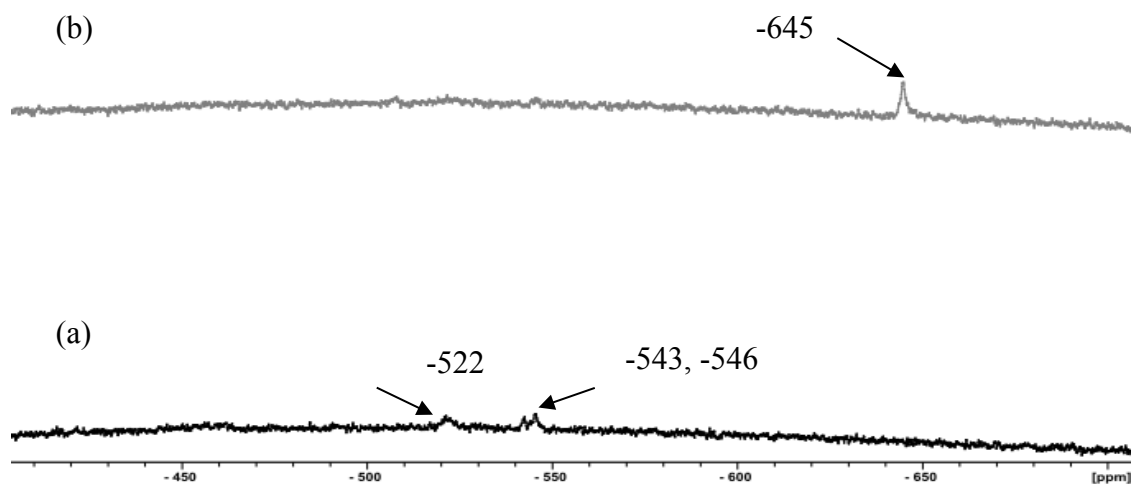


Fig. S7 ^{51}V NMR spectrum of **1** (0.61 mM) in a 3:2 mixture of $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$ (a) and after addition of 1 equivalent of H_2O_2 (b).

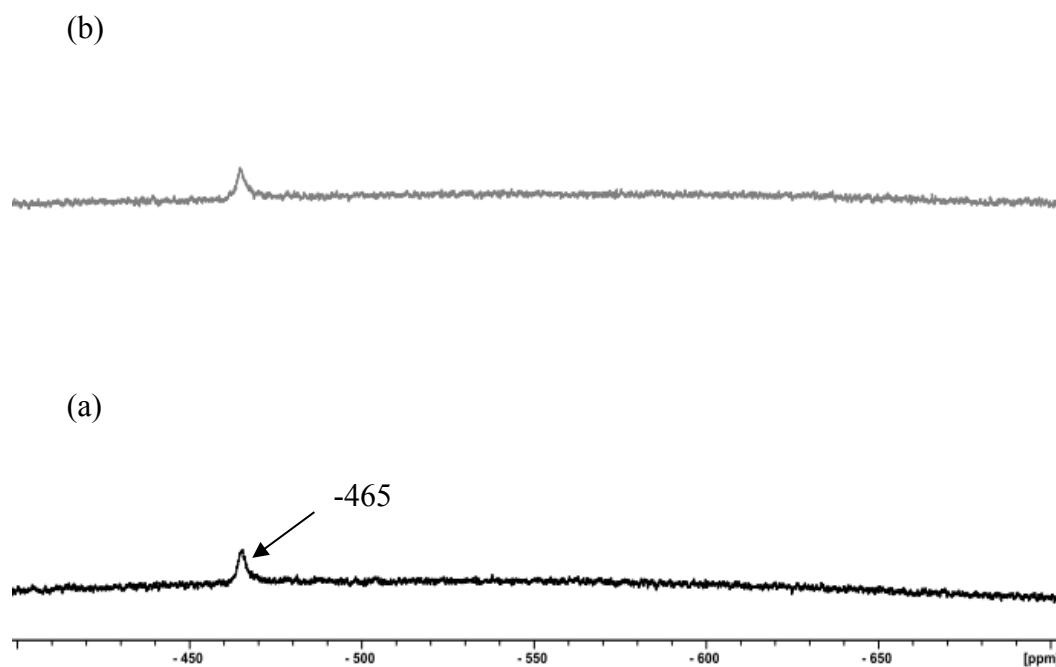


Fig. S8 ^{51}V NMR spectrum of **1** (0.62 mM) in a 3:2 mixture of $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$ (a) and after addition of 8 equivalents of H_2O_2 (b).

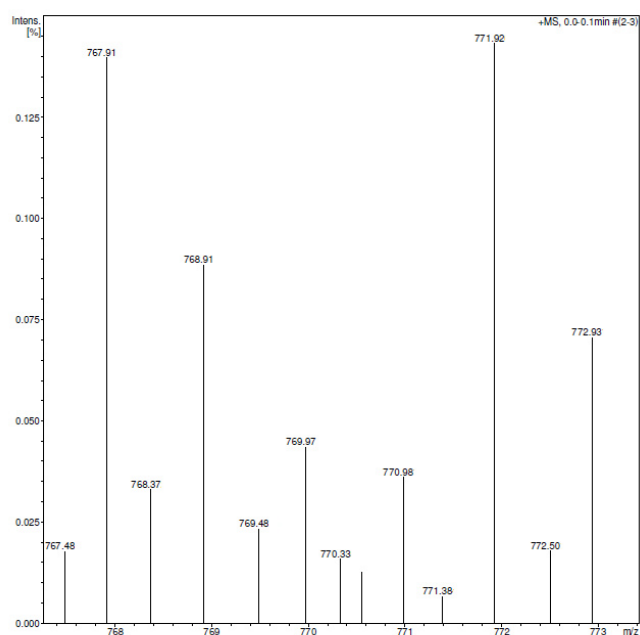


Fig. S9 ESI-MS spectrum of the reaction mixture containing 10 mL of a 1.0×10^{-1} M catechol solution mixed with 5.0 mL of a 4.0×10^{-4} M solution of $[V^V O(OMe)(MeOH)(L^1)]$ (**2**) in an atmosphere of air.

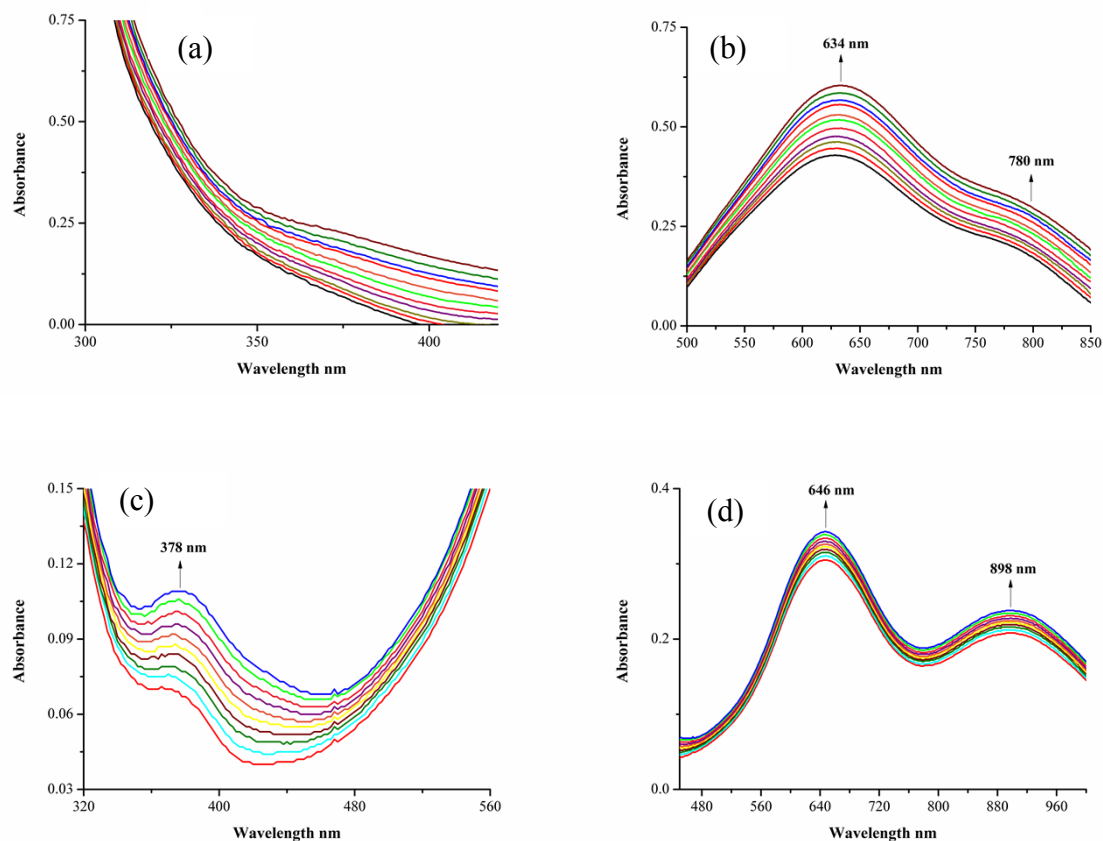


Fig. 10 Spectral changes observed during the reaction of 3,5-di-tert-butylcatechol with $[\text{V}^{\text{VO}}(\text{OMe})(\text{MeOH})(\text{L}^1)]$ **2**. Reaction Conditions for (a) and (b): 3,5-di-tert-butylcatechol solution (10.0 mL, 1.0×10^{-2} M) mixed with 5.0 mL solution of $[\text{V}^{\text{VO}}(\text{OMe})(\text{MeOH})(\text{L}^1)]$ (4.0×10^{-4} M) in an atmosphere of air. The spectra were recorded at every six min intervals. For (c) and (d): 3,5-di-tert-butylcatechol solution (10.0 mL, 1.0×10^{-2} M) mixed with 5.0 mL (4.0×10^{-5} M) solution of $[\text{V}^{\text{VO}}(\text{OMe})(\text{MeOH})(\text{L}^1)]$ in an atmosphere of air. The spectra were recorded at every 12 min intervals.