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Bromoperoxidase mimics as catalysts for oxidative bromination — Synthesis, Structures and Properties of the diversified oxidation state of vanadium (III, IV and V) complexes with pincer-N-heterocycle ligands

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Table S1. The deviations of the coordinated atoms out of equatorial plane for **1-5**

1		**2**		**3**		**4**		**5**	
V	-0.0088(14)	V	0.4435(22)	V1	-0.0878(14)	V	-0.2738(16)	V	-0.3733(14)
O2	0.0000	O	2.0320(37)	O1	0.5165(18)	O1	-1.8658(29)	O1	-1.9640(27)
O3	0.0000	N3	-0.2321(21)	O2	1.9732(27)	O2	1.9485(29)	O2	1.8224(27)
N5	1.9807(27)	N7	-1.7060(42)	O3	-0.2415(17)	O3	0.0105(11)	O3	0.1048(10)
N1	0.0000	N2	-0.2226(20)	O4	-2.0678(27)	N1	0.0164(18)	N1	0.1662(16)
N6	-1.9961(28)	N5	0.2260(20)	N1	0.4646(20)	N4	-0.0130(14)	N4	-0.1343(13)
		N6	0.2287(21)	N5	-0.6358(19)	N2	-0.0139(15)	N2	-0.1367(13)
				N7	-0.1038(17)				

Table S2. Eigenvalues (in Hartree) of HOMO and LUMO orbitals (a.u) and the gaps (eV) between them of the complexes **1-5**.

Complex	**1**	**2**	**3**	**4**	**5**
HOMO	-0.2625	-0.1819	-0.1850	-0.1829	-0.1773
LUMO	-0.1495	-0.1818	-0.1834	-0.1827	-0.1769
Gap	3.074	0.002	0.037	0.005	0.009

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Table S3. The atomic net charge for the complexes calculated at the PBE level.

1		**2**		**3**		**4**		**5**	
V1	0.724	V	0.422	V1	0.554	V	1.113	V	1.101
O2	-0.481	O	-0.539	O1	-0.481	O1	-0.571	O1	-0.604
O3	-0.471	N3	-0.201	O2	-0.489	O2	-0.608	O2	-0.566
N5	-0.197	N7	-0.432	O3	-0.467	O3	-0.541	O3	-0.571
N1	-0.513	N2	-0.208	O4	-0.471	N1	-0.417	N1	-0.284
N6	-0.199	N5	-0.185	N1	-0.450	N4	-0.291	N4	-0.282
		N6	-0.181	N5	-0.185	N2	-0.312	N2	-0.135
				N7	-0.218				

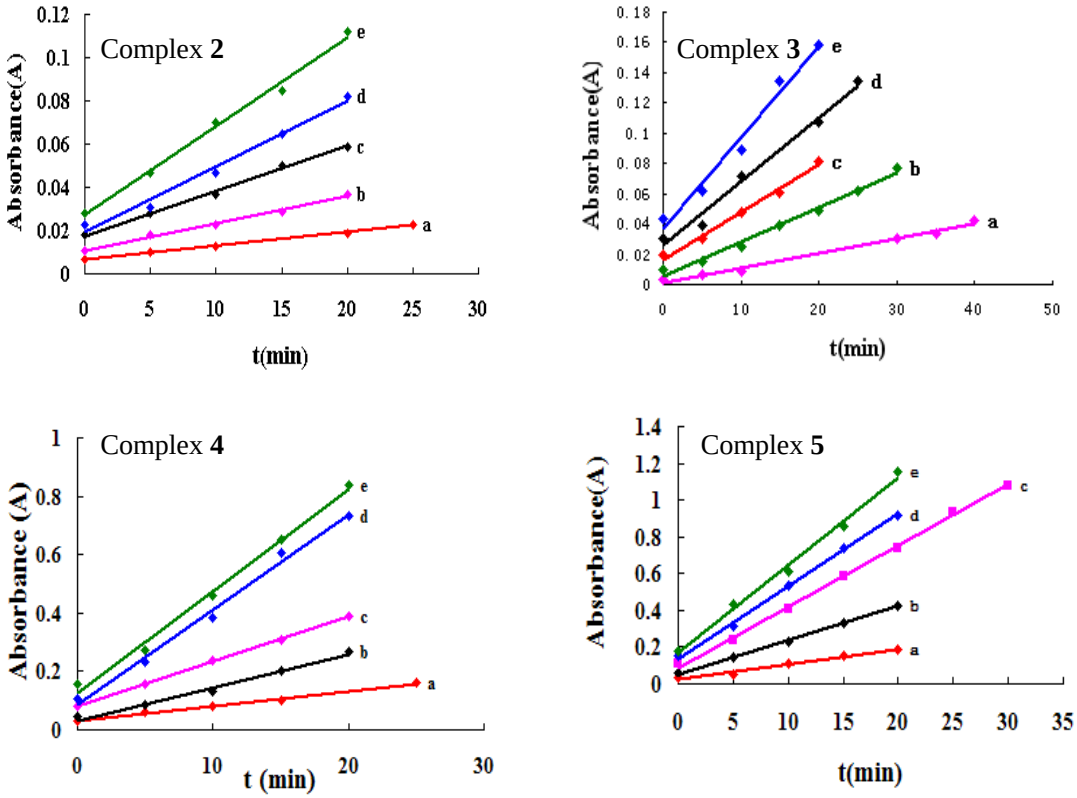

Fig. S1 The measurable absorbance dependence of time for the complexes **2-5**. Conditions used: pH = 5.8, c(KBr) = 0.4 mol/L, c(H_2O_2) = 1 mmol/L, c(phenol red) = 10^{-4} mol/L. c(complex **2**/mmol/L) = a: 1.53×10^{-2}; b: 3.01×10^{-2}; c: 4.58×10^{-2}; d: 6.11×10^{-2}; e: 7.64×10^{-2}. c(complex **3**/mmol/L) = a: 7.39×10^{-3}; b: 1.48×10^{-2}; c: 2.22×10^{-2}; d: 2.96×10^{-2}; e: 3.69×10^{-2}. c(complex **4**/mmol/L) = a: 1.96×10^{-2}; b: 3.92×10^{-2}; c: 5.89×10^{-2}; d: 9.81×10^{-2}; e: 1.18×10^{-1}; e: 1.06×10^{-1}. c(complex **5**/mmol/L) = a: 1.87×10^{-2}; b: 3.75×10^{-2}; c: 5.62×10^{-2}; d: 7.49×10^{-2}; e: 9.37×10^{-1}.

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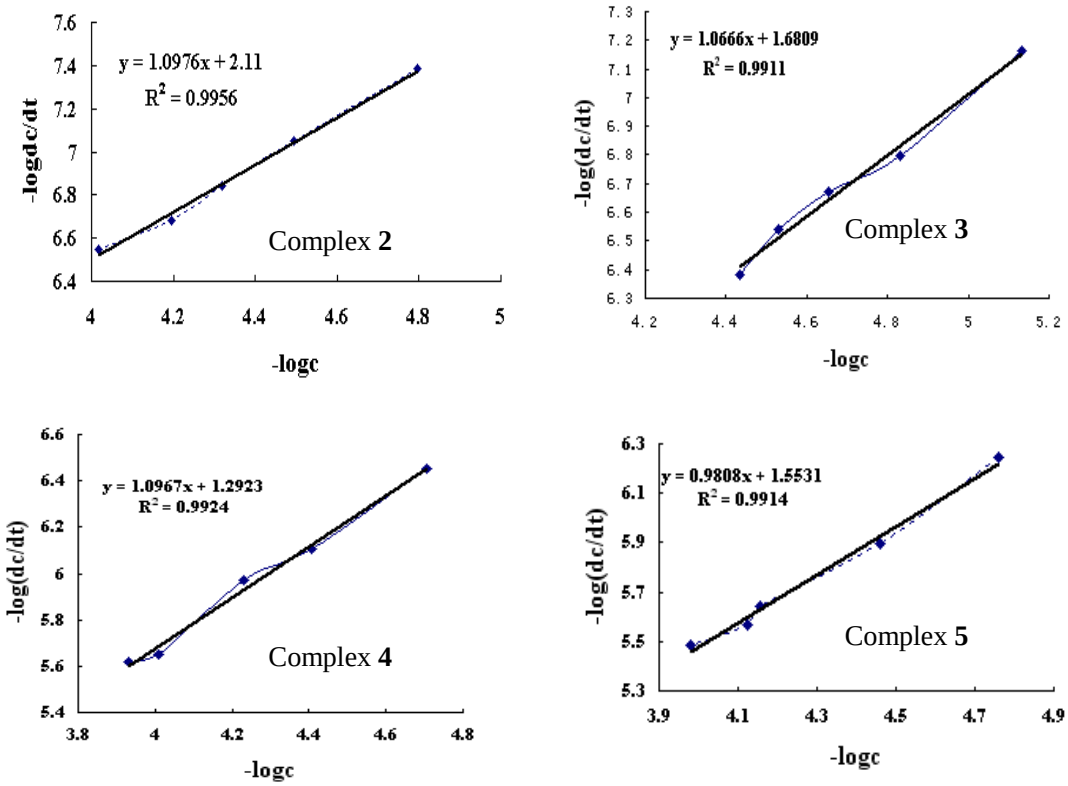

Fig. S2 *–log(dc/dt)* dependence of *–logc* for **2-5** in DMF–H_2O at 30 ± 0.5 °C (c is the concentration of the oxidovanadium complex **2-5**; Conditions used: c(phosphate buffer) = 50 mmol/L, pH = 5.8, c(KBr) = 0.4 mol/L, c(phenol red) = 10^{-4} mol/L.