Supplementary Information

The intricate paramagnetic state of $[Os(Q)_2(bpy)]^+$, Q = 4,6-di-*tert*-butyl-*o*-iminobenzoquinone

Dipanwita Das,[a] Thomas Michael Scherer,[b] Amit Das,[a] Tapan Kumar Mondal,[c] Shaikh M. Mobin,[a] Jan Fiedler,[d] José Luis Priego,[e] Reyes Jiménez-Aparicio,[*e] Wolfgang Kaim,[*b] and Goutam Kumar Lahiri[*a]

[a]*Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India. E-mail: lahiri@chem.iitb.ac.in*

[b]*Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany. E-mail: kaim@iac.uni-stuttgart.de*

[c]*Department of Chemistry, Jadavpur University, Jadavpur, Kolkata-700032, India*

[d]*J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic*

[e]*Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, Ciudad Universitaria, E-28040 Madrid, Spain*

Table S1 Calculated energy

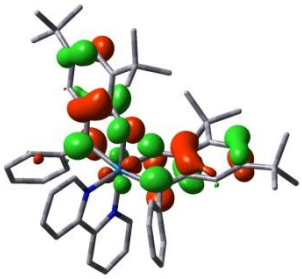
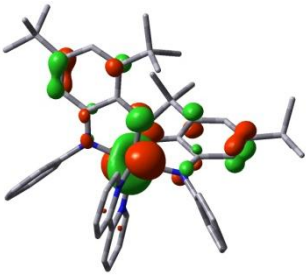
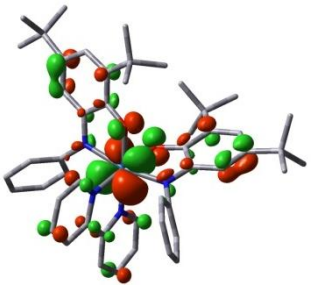
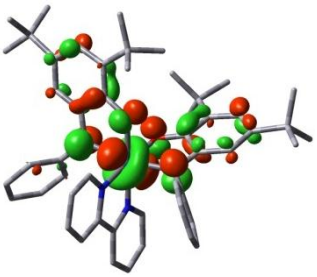
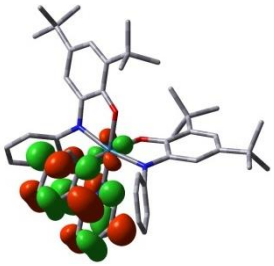
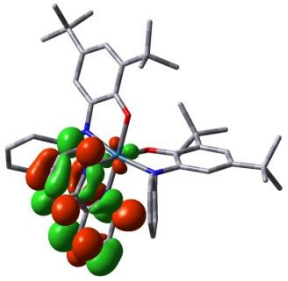
$\mathbf{1}^{+}$		$\mathbf{1}^{2+}$		**1**	
S = 1/2	S = 3/2	S = 0	S = 1	S = 0	S = 1
–2400.35904646 a.u.	–2400.33965818 a.u.	–2400.07040917 a.u.	–2400.04976041 a.u.	–2400.53698675 a.u.	–2400.52957060 a.u.
E(S =1/2) –E(S=3/2)=–0.01938828 a.u. =–12.166 kcal/mol =–4255.24 cm^{-1}		E(S =0)-E(S=1) = –0.02064876 a.u. = –12.957 kcal/mol = –4531.88 cm^{-1}		E(S =0)-E(S=1) = –0.00741615 a.u. = –4.6537 kcal/mol = –1627.66 cm^{-1}	

Table S2 Selected experimental bond angles (^{o}) for [**1**]ClO_4 and calculated bond angles for $\mathbf{1}^{+}$, $\mathbf{1}^{2+}$, **1** and $\mathbf{1}^{-}$

Bond angles	$\mathbf{1}^{+}$(*S*=1/2)		$\mathbf{1}^{2+}$(*S*=0)	**1**(*S*=0)	$\mathbf{1}^{-}$(*S*=1/2)
	X-ray	DFT	DFT	DFT	DFT
N1-Os1-O1	78.78(16)	77.21	76.21	78.19	77.76
N1-Os1-O2	91.93(16)	91.42	90.70	91.24	89.28
N1-Os1-N2	168.09(18)	165.2	161.1	165.2	162.7
N1-Os1-N3	101.73(17)	98.26	98.07	100.2	99.68
N1-Os1-N4	93.62(18)	93.57	96.65	90.67	93.07
N2-Os1-O1	93.21(15)	93.07	90.71	91.41	90.76
N2-Os1-O2	79.02(17)	77.18	76.22	78.28	77.90
N2-Os1-N3	87.44(17)	92.47	96.61	90.89	93.10
N2-Os1-N4	95.75(18)	98.61	98.06	100.5	100.9
N3-Os1-O1	171.94(19)	172.6	170.2	175.0	173.0
N3-Os1-O2	98.96(17)	96.99	94.69	97.99	95.81
N3-Os1-N4	77.90(18)	77.53	77.91	77.21	77.85
N4-Os1-O1	94.04(17)	96.77	94.71	98.06	95.76
N4-Os1-O2	174.09(19)	173.0	170.2	175.0	173.5
O1-Os1-O2	89.04(15)	89.03	77.91	86.75	90.63

Table S3 Selected molecular orbitals along with their energies and compositions for $\mathbf{1}^{+}$ in doublet (*S*=1/2) state

MO	Energy (eV)	% of Composition		
		Q	bpy	Os
α-spin				
LUMO+5	-2.56	94	01	05
LUMO+4	-2.77	85	03	12
LUMO+3	-3.72	01	95	04
LUMO+2	-3.86	02	94	04
LUMO+1	-4.78	02	91	07
LUMO	-5.34	61	04	35
SOMO	-7.07	92	02	06
HOMO-1	-7.61	41	04	55
HOMO-2	-7.99	37	13	50
HOMO-3	-8.39	55	03	42
HOMO-4	-8.51	89	02	09
HOMO-5	-8.79	75	03	22
HOMO-6	-8.98	92	02	06
HOMO-7	-9.18	96	01	03
HOMO-8	-9.27	98	01	01
HOMO-9	-9.29	99	0	01
HOMO-10	-9.68	01	98	01
β-spin				
LUMO+5	-2.75	84	03	13
LUMO+4	-3.72	01	95	04
LUMO+3	-3.85	02	93	05
LUMO+2	-4.77	03	89	08
LUMO+1	-4.99	76	03	21
LUMO	-5.70	91	03	06
HOMO	-7.54	47	04	49
HOMO-1	-7.85	40	13	47
HOMO-2	-8.32	45	04	51
HOMO-3	-8.39	84	03	13
HOMO-4	-8.70	68	03	29
HOMO-5	-8.93	94	02	04
HOMO-6	-9.17	95	01	04
HOMO-7	-9.26	98	01	01
HOMO-8	-9.27	99	0	01
HOMO-9	-9.68	01	98	01
HOMO-10	-10.01	97	01	02

		
SOMO	HOMO-1	HOMO-2
		
LUMO	LUMO+1	LUMO+2
Contor plots of selected MOs (α-spin) of $\mathbf{1}^{+}$		

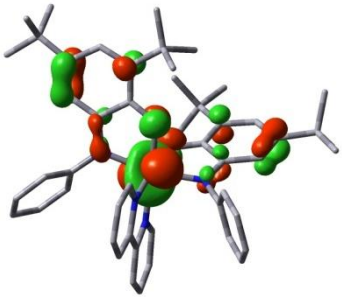
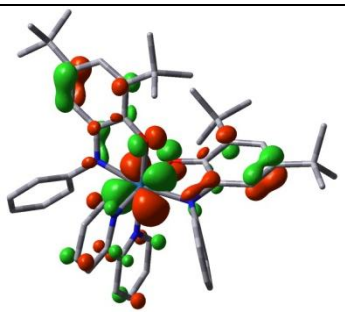
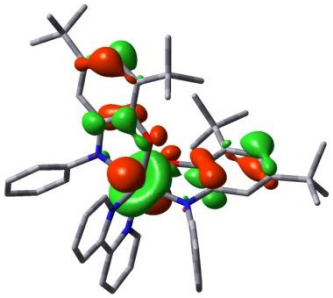
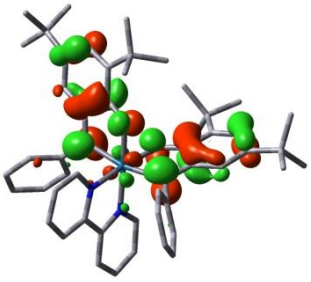
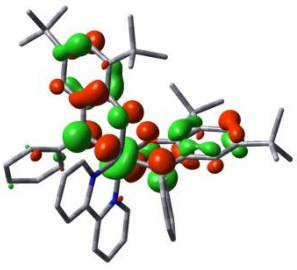
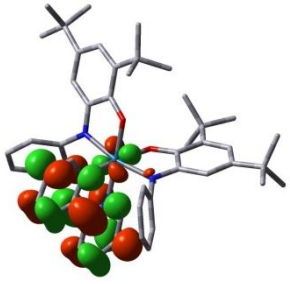
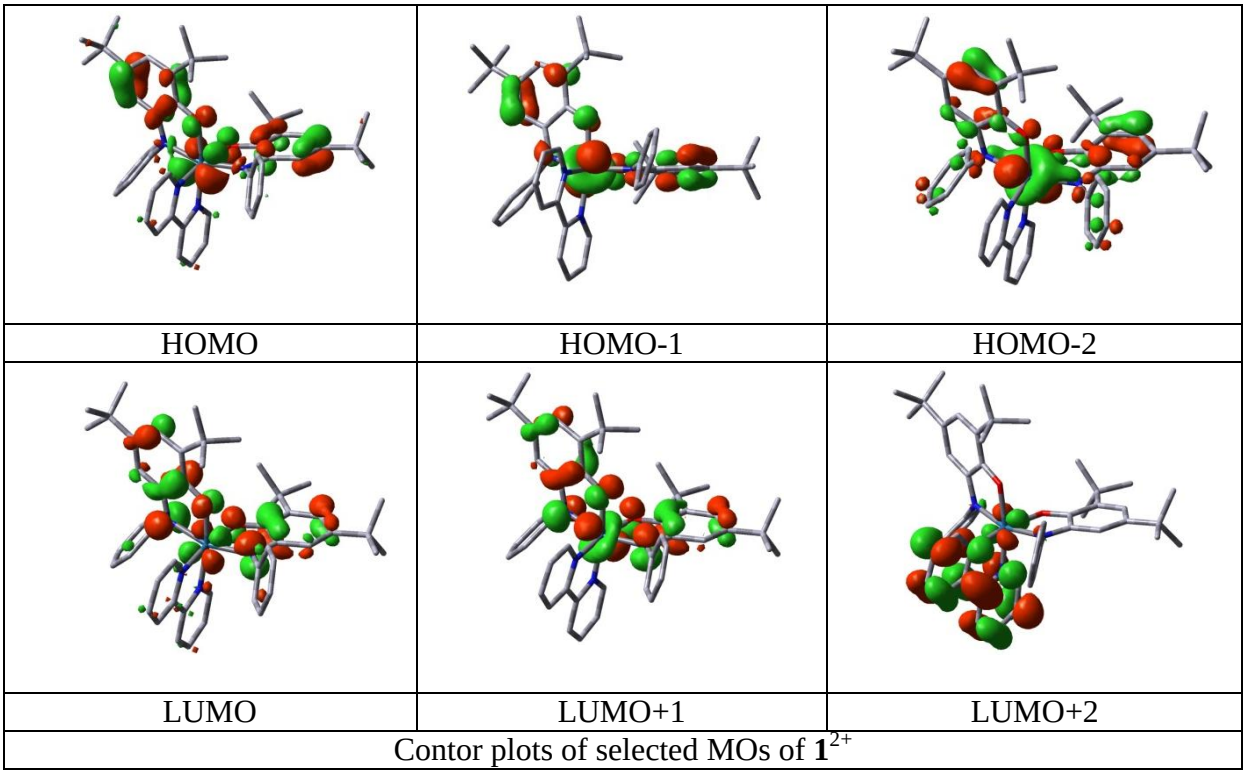
		
HOMO	HOMO-1	HOMO-2
		
LUMO	LUMO+1	LUMO+2
Contor plots of selected MOs (β-spin) of $\mathbf{1}^{+}$		

Table S4 Selected molecular orbitals along with their energies and compositions for $\mathbf{1}^{2+}$ in singlet (*S*=0) state

MO	Energy (eV)	% of Composition		
		Q	bpy	Os
LUMO+5	-5.45	74	02	24
LUMO+4	-6.40	01	96	03
LUMO+3	-6.48	02	94	04
LUMO+2	-7.43	04	88	08
LUMO+1	-8.41	74	02	24
LUMO	-8.67	79	09	12
HOMO	-10.79	66	07	27
HOMO-1	-10.85	51	03	46
HOMO-2	-11.26	58	04	38
HOMO-3	-11.56	87	03	10
HOMO-4	-11.56	70	02	28
HOMO-5	-11.66	85	05	10
HOMO-6	-11.77	96	02	02
HOMO-7	-11.82	97	01	02
HOMO-8	-11.94	81	02	17
HOMO-9	-12.33	02	97	01
HOMO-10	-12.81	98	01	01

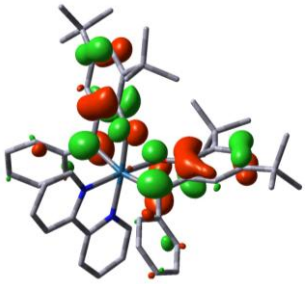


HOMO	HOMO-1	HOMO-2
LUMO	LUMO+1	LUMO+2

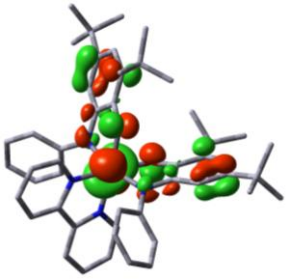
Contor plots of selected MOs of $\mathbf{1}^{2+}$

Table S5 Energy and composition of some selected MOs of **1** in singlet (*S*=0) state

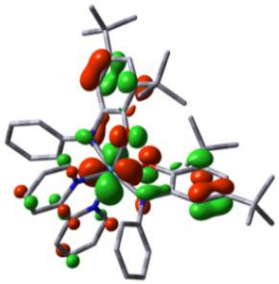
MO	energy (eV)	% of composition		
		Q	bpy	Os
LUMO+5	0.02	87	02	11
LUMO+4	-0.07	89	01	10
LUMO+3	-1.20	04	90	06
LUMO+2	-1.34	02	92	06
LUMO+1	-2.22	04	85	11
LUMO	-2.23	54	08	38
HOMO	-4.03	96	01	03
HOMO-1	-4.58	53	03	44
HOMO-2	-5.05	50	14	36
HOMO-3	-5.45	66	09	25
HOMO-4	-5.48	55	03	42
HOMO-5	-5.76	65	03	32
HOMO-6	-6.20	99	0	01
HOMO-7	-6.49	95	01	04
HOMO-8	-6.71	98	01	01
HOMO-9	-6.73	99	0	01
HOMO-10	-7.14	90	05	05



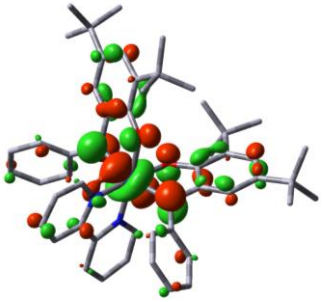
HOMO



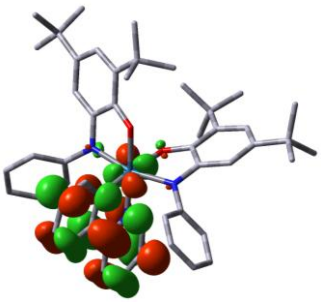
HOMO-1



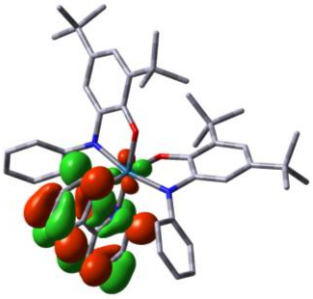
HOMO-2



LUMO



LUMO+1

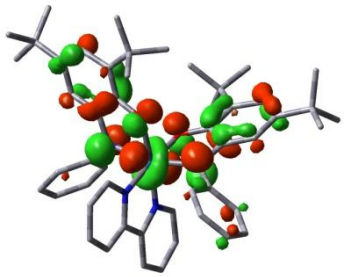
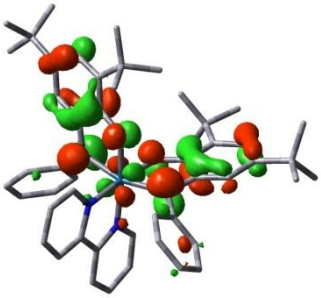
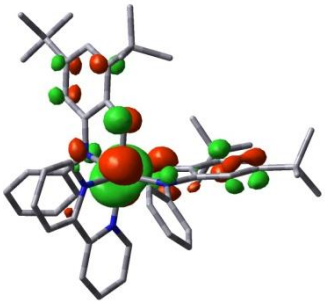
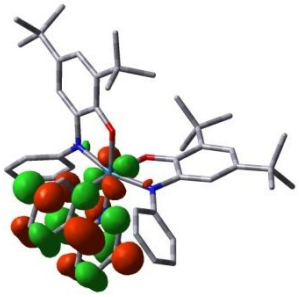
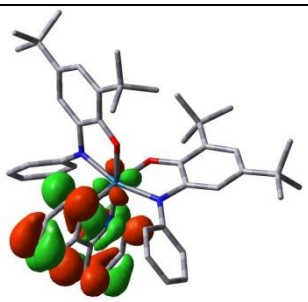
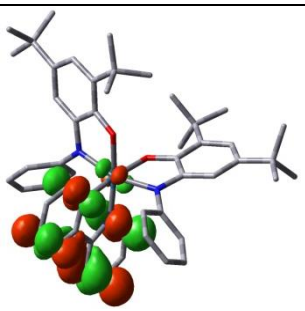
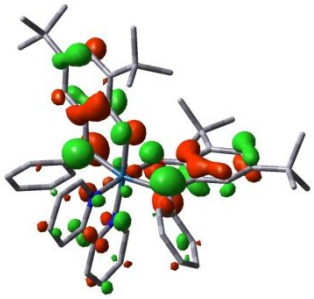
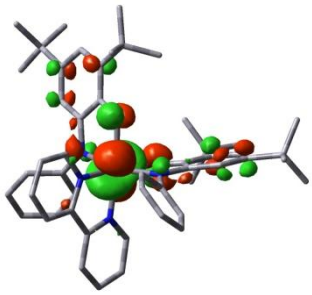
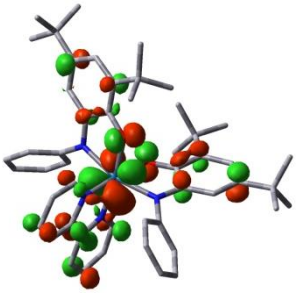
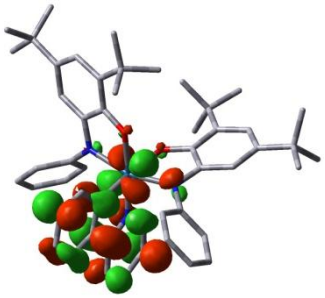
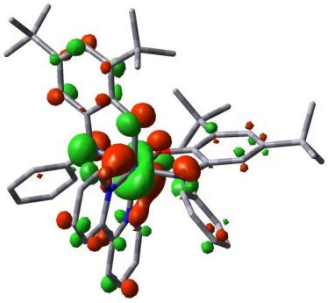
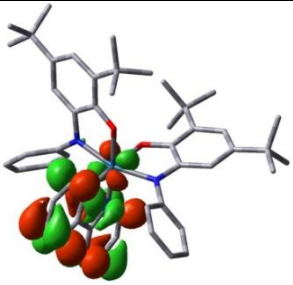


LUMO+2

Contor plots of selected MOs of **1**

Table S6 Selected molecular orbitals along with their energies and compositions for **1**$^{-}$ in doublet (*S*=1/2) state

MO	Energy (eV)	% of Composition		
		Q	bpy	Os
α-spin				
LUMO+5	2.64	66	01	33
LUMO+4	2.54	86	03	11
LUMO+3	5.50	79	01	20
LUMO+2	1.66	01	94	05
LUMO+1	1.57	02	91	07
LUMO	0.69	04	84	12
SOMO	-0.74	76	02	22
HOMO-1	-1.20	86	07	07
HOMO-2	-1.78	41	05	54
HOMO-3	-2.25	50	16	34
HOMO-4	-2.73	76	06	18
HOMO-5	-2.85	55	06	39
HOMO-6	-2.99	67	03	30
HOMO-7	-3.49	97	01	02
HOMO-8	-3.79	95	02	03
HOMO-9	-4.04	98	01	01
HOMO-10	-4.18	79	20	01
β-spin				
LUMO+5	2.59	90	02	08
LUMO+4	2.52	73	03	24
LUMO+3	1.68	07	82	11
LUMO+2	1.61	03	86	11
LUMO+1	0.82	51	17	32
LUMO	0.72	10	69	21
HOMO	-0.84	79	16	05
HOMO-1	-1.53	40	06	54
HOMO-2	-1.95	45	17	38
HOMO-3	-2.15	60	04	36
HOMO-4	-2.56	84	05	11
HOMO-5	-2.83	73	03	24
HOMO-6	-3.43	98	01	01
HOMO-7	-3.75	96	02	02
HOMO-8	-4.02	99	01	0
HOMO-9	-4.17	86	12	02
HOMO-10	-4.19	91	05	04

		
SOMO	HOMO-1	HOMO-2
		
LUMO	LUMO+1	LUMO+2
Contour plots of selected MOs (α-spin) of **1**$^{-}$		
		
HOMO	HOMO-1	HOMO-2
		
LUMO	LUMO+1	LUMO+2
Contor plots of selected MOs (β-spin) of **1**$^{-}$		

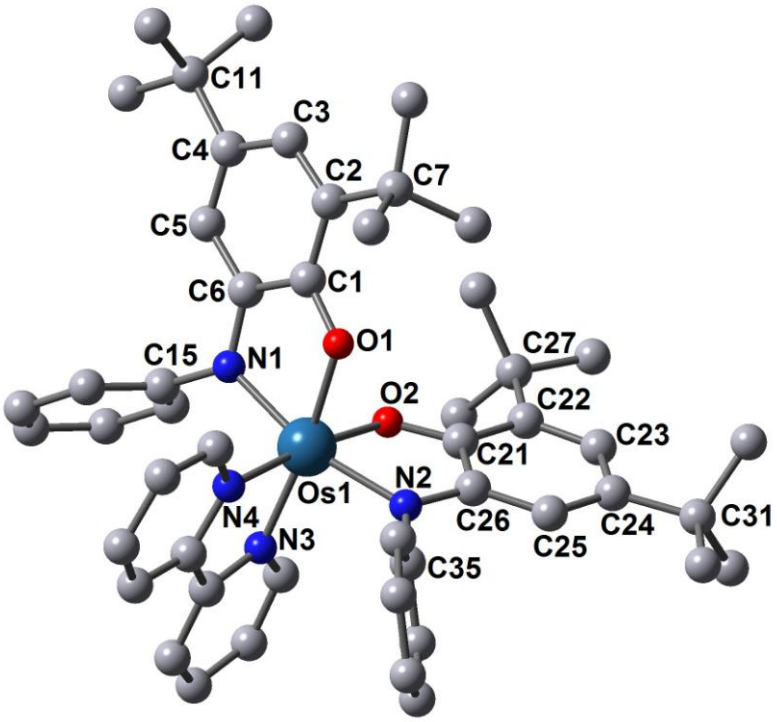


Fig. S1 Optimised structure of $\mathbf{1}^{+}$.

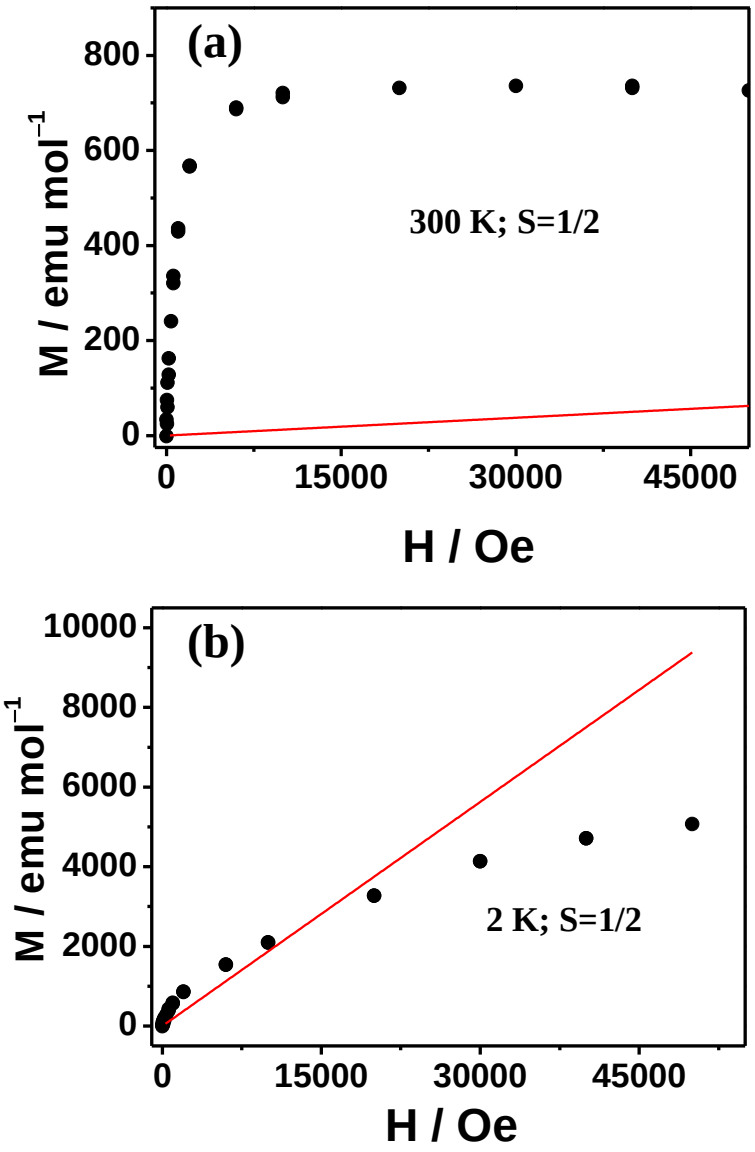


Fig. S2 Representation of the magnetisation towards magnetic field from 0 to 5 T of [**1**]ClO_4 measured at (a) 300 K and (b) 2 K. Solid line represents the calculated curve for S = 1/2 spin system.

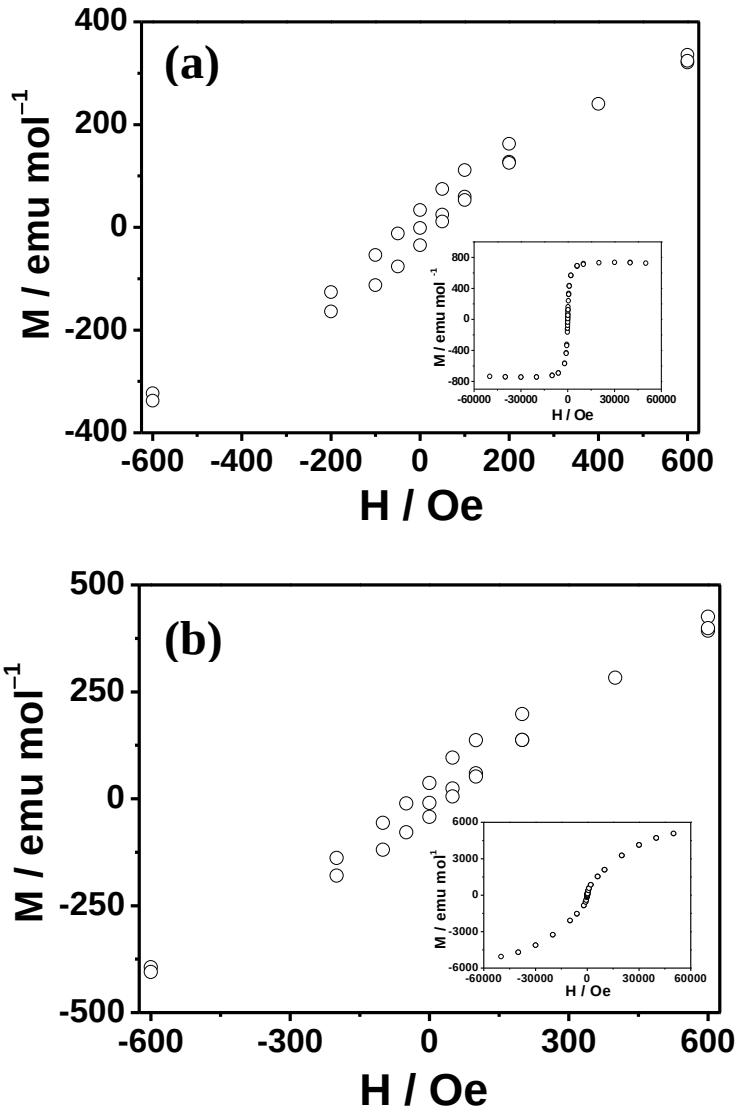


Fig. S3 Detail of the loop at (a) 300 K and (b) 2 K showing hysteresis. Inset shows the complete curve from 5 to –5 T.