Electronic Supplementary Information

A dinuclear iron complex with a single oxo bridge as an efficient water-oxidizing catalyst in the presence of cerium(IV) ammonium nitrate: New findings and the current controversies

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Table of Contents

1. Material and methods

K_2FeO_4 and tris(2-pyridylmethyl)amine purchased were purchased from commercial sources and were used without further purification.

X-ray diffraction experiment: single crystal of **1** in form of red block was chosen and mounted on a Stoe IPDS2t diffractometer equipped with MoK_α radiation source (see Table S1 for basic crystallographic details). Problems connected with limited crystals quality and the presence of weak reflections had to be faced. As a consequence, it was not possible to optimize the weighting scheme to obtain GooF values near 1.0.

Details of structure refinement: Atomic coordinates for the structure model for the reported isomorphous compound ($[\{Fe(tpa)(H_2O)\}_2O](ClO_4)_4 \cdot 3H_2O \cdot 0.25C_2H_5OH$ (tpa = tris(2-pyridylmethyl)amine))[1] were retrieved from the CCDC database and used as a starting model for subsequent refinement in SHELXL software.[2] There are four symmetry-independent formula units. In the course of refinement ethanol of solvation C atoms were removed. The remaining O atom seems to be present and disordered in two positions with half-occupancies (EADP restraints had to be applied). Moreover, three additional water molecules (O1W, O2W, O3W) had to be introduced, where O3W is disordered in two positions (EADP restraints had to be applied; the final refined occupancies: 0.63(1) and 0.37(1), respectively).

Additionally, in the case of two perchlorate anions modeling of disorder was introduced. It was assumed that the anions adopt two positions related by rotation of all O atoms, conserving the position of the Cl atom. For the Cl14-anion DFIX restraints were used for the Cl-O bond lengths (1.430(5) Å) and for O…O distances (2.35(1) Å), along with EADP restraints for all corresponding O atoms in the two disorder components. The final refined occupancies were 0.64(1) and 0.36(1), respectively. For the Cl15-anion soft SADI restraints were used for all Cl-O bond lengths with EADP/ISOR restraints for part of the disordered O atoms. The final refined occupancies were 0.56(1) and 0.44(1), respectively.

C-bonded H atoms were generated in their calculated positions and a riding model with U_{eq} = $1.2U_{eq}$ (parent C atom) was used. Part of the O-bonded H atoms was located on difference Fourier maps and initially refined with DFIX restraints setting O-H bond lengths at 0.820(2) Å and the water H…H distances at 1.50(1) Å. Subsequently the H atoms parameters were constrained.

On the final difference Fourier map the highest peak of 0.56 e/Å^3 is located at 0.60 Å from O67 atom of the disordered perchlorate anion (with Cl14).

CCDC-955723 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1.1 Synthesis of the complex 1:[1,3]

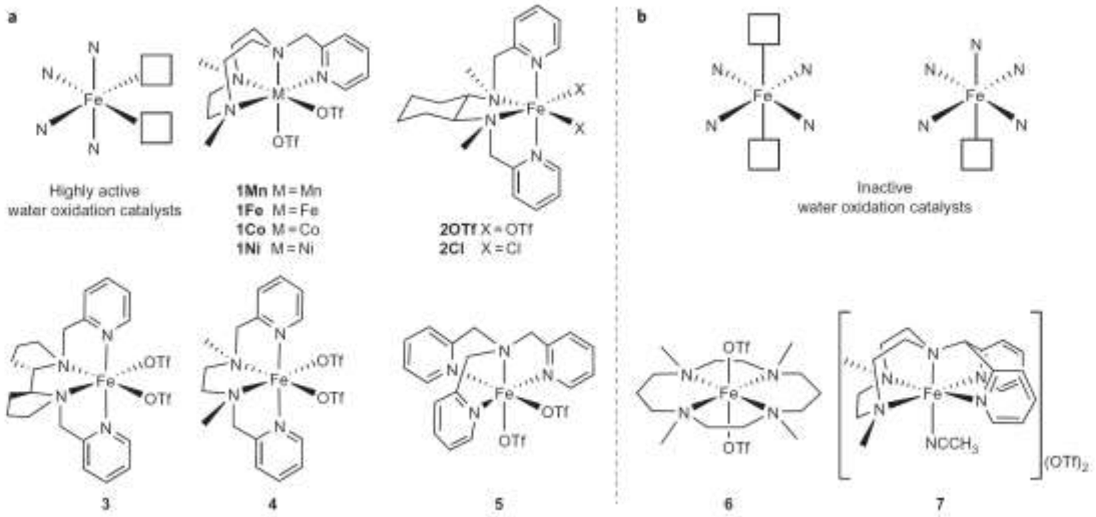
A mixture of tpa·3HClO$_4$ (0.2 g, 0.35 mmol; tpa = tris(2-pyridylmethyl)amine) and triethylamine (0.12 g, 1.2 mmol) dissolved in methanol (7 mL) was added to Fe(C1O$_4$)$_3$·6H$_2$O (0.19 g, 0.4 mmol) dissolved in water : methanol (1:1, 3 mL) to produce a red solution. Red crystals of **1** were deposited over a few hours.

1.2 The complex on montmorillonite

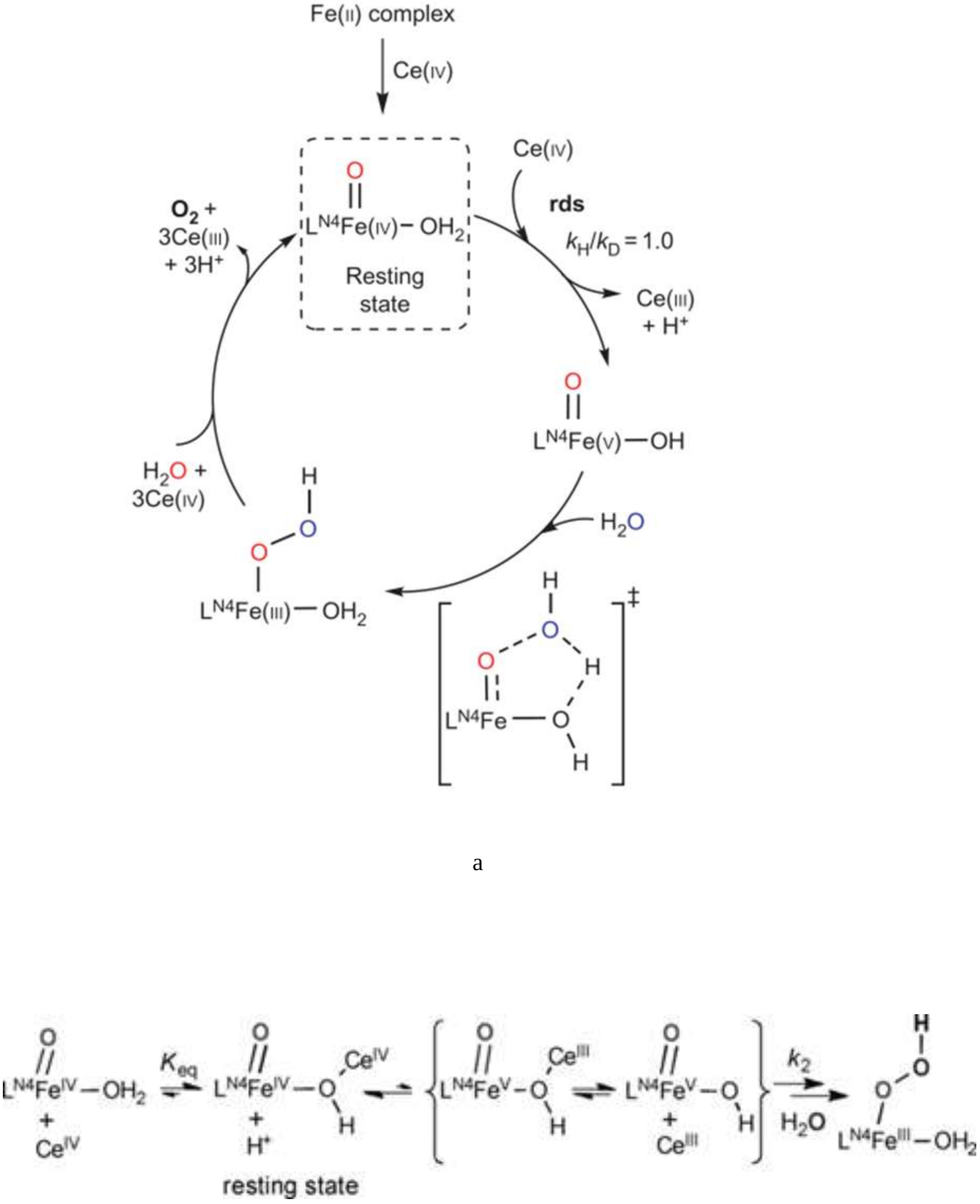
Na-montmorillonite clay (1.0 g) was added to an aqueous solution of the complex **1** (~ 1.0 mM, 10 ml). After stirring for 30 min, the complex-clay hybrid was filtered off, washed with water and then dried in air.

2. Water Oxidation

Oxygen evolution from the aqueous solutions in the presence of $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 ºC in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continuously with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with Ce(IV) solution. Without catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, compounds were added, and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S1). The formation of oxygen followed, and oxygen formation rates per iron site were obtained from linear fits of the data.



Scheme S1 Efficient Fe complexes for water oxidation (a). Complexes with two or only one available *trans* coordination site are inactive for water oxidation (b). Water oxidation by the complexes is performed in the presence of Ce(IV). Image and caption from ref. 13.



b

Scheme S2 Proposed mechanism for water oxidation by the Fe complex reported by Fillol, Costas and Co-workers. Image and caption from ref. 13. (a). In this mechanism, Ce(IV)-OH may also play an important role. Image and caption from ref. 12.

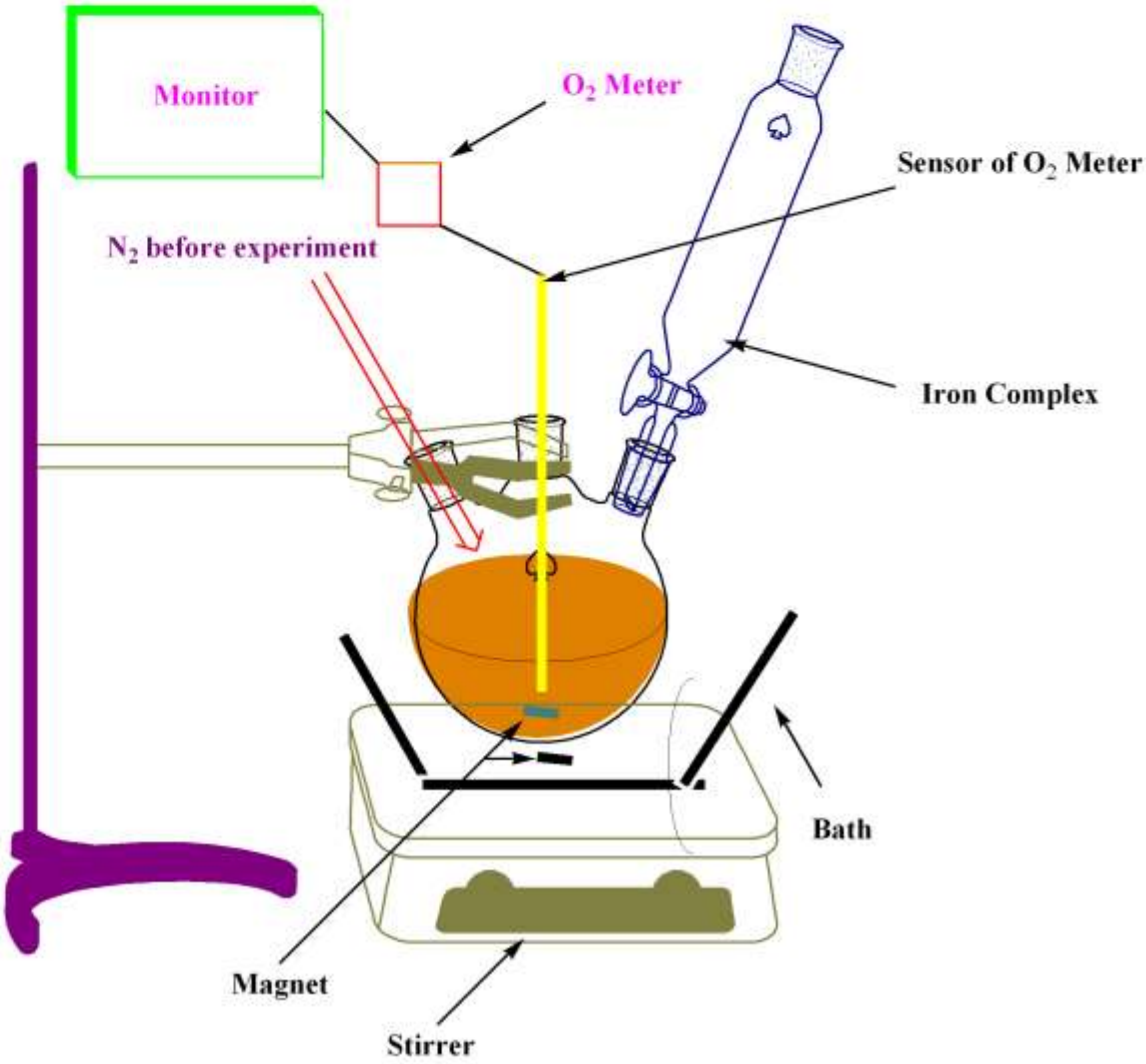


Fig. S1 The reactor setup for oxygen evolution experiment from aqueous solution in the presence of Ce(IV) and **1** or FeO_4^{2-} ions.

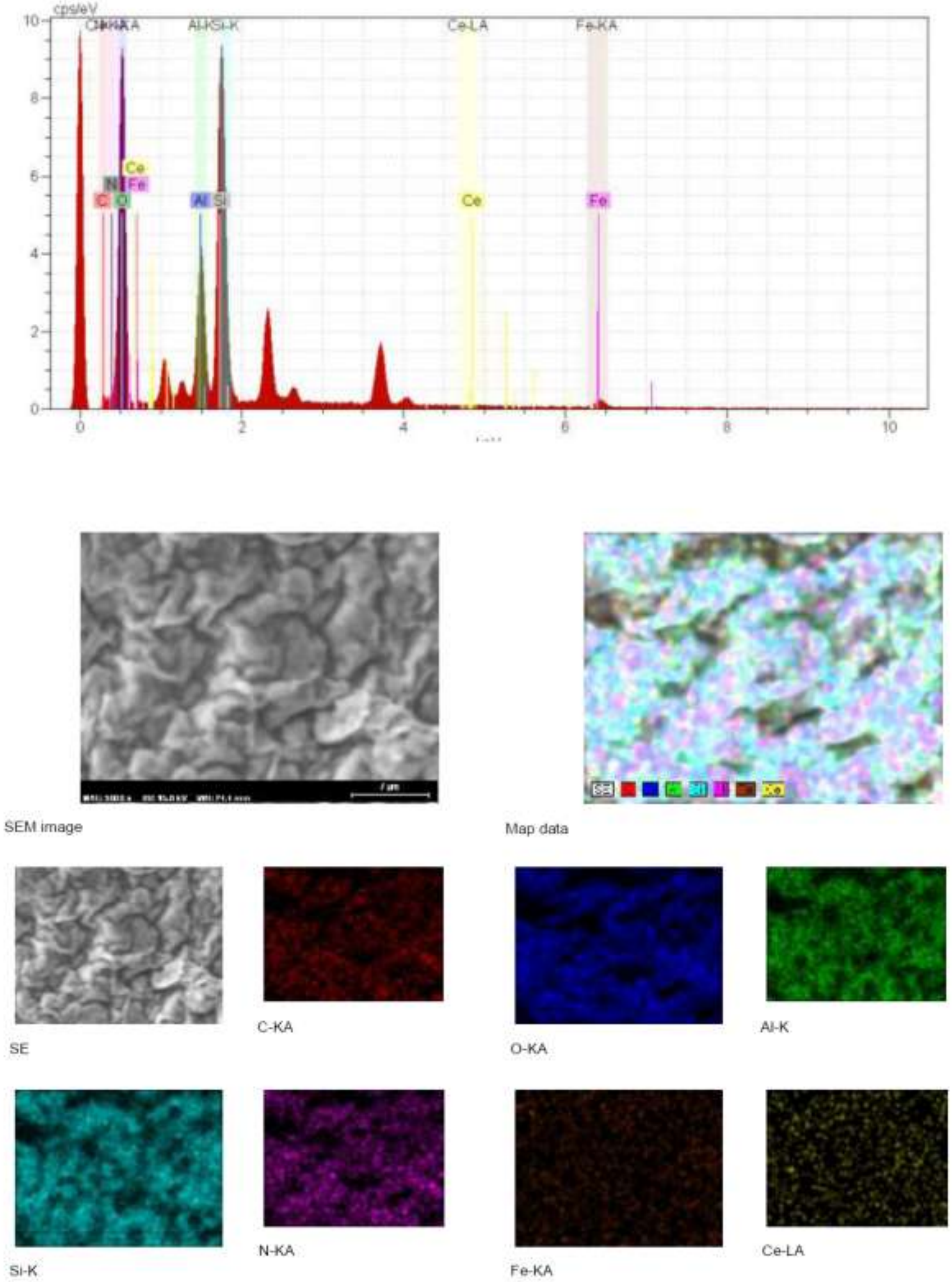
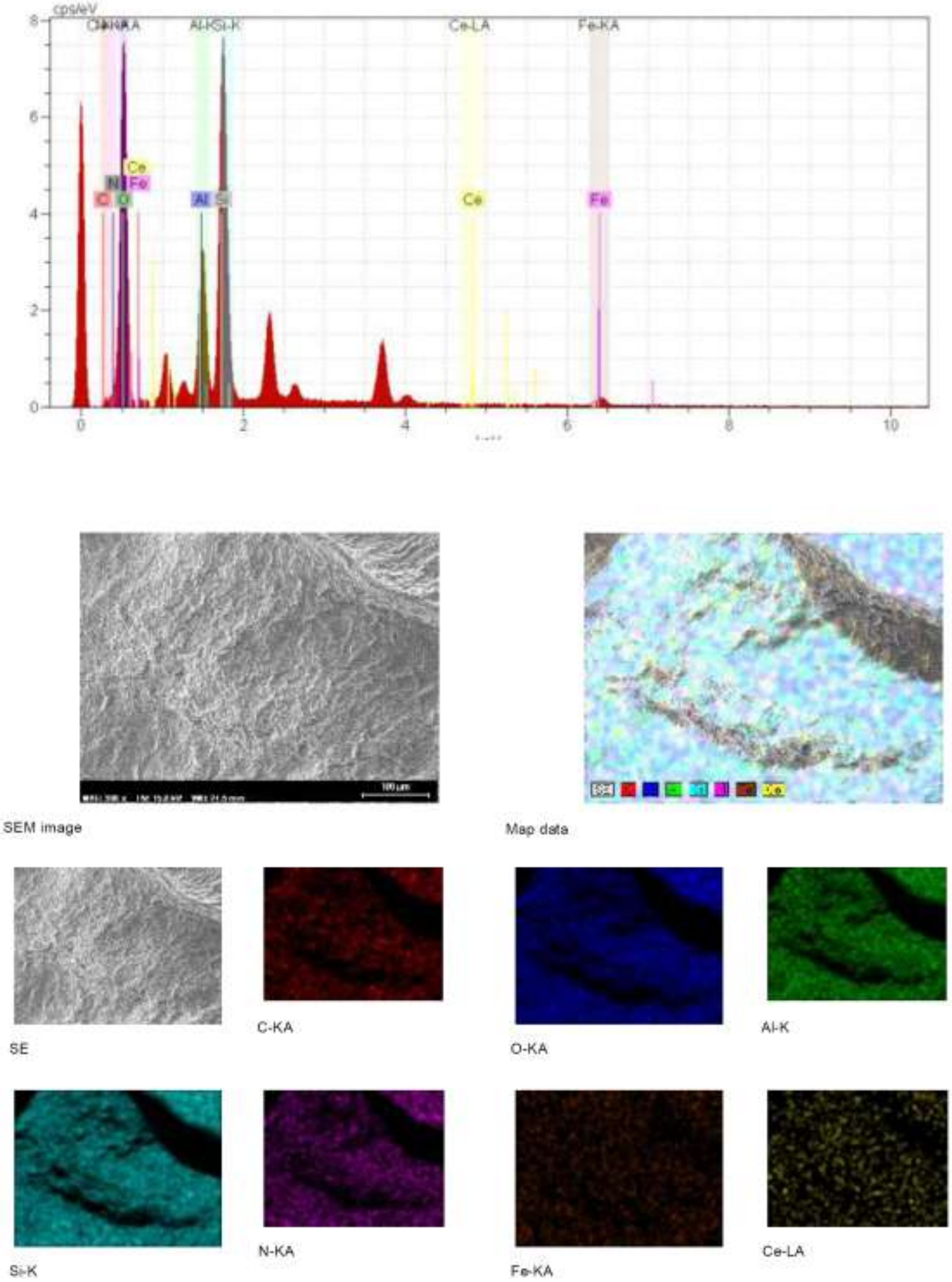


Fig. S2 EDX- SEM (×5000) results from **1** on montmorillonite.



SEM image

Map data

SE

C-KA

O-KA

Al-K

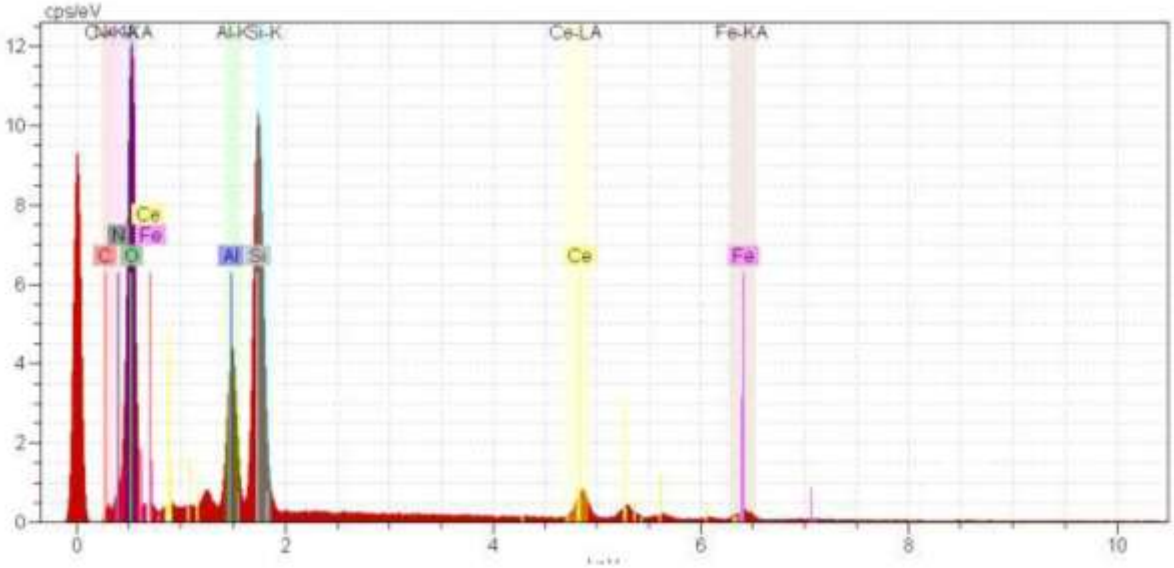
Si-K

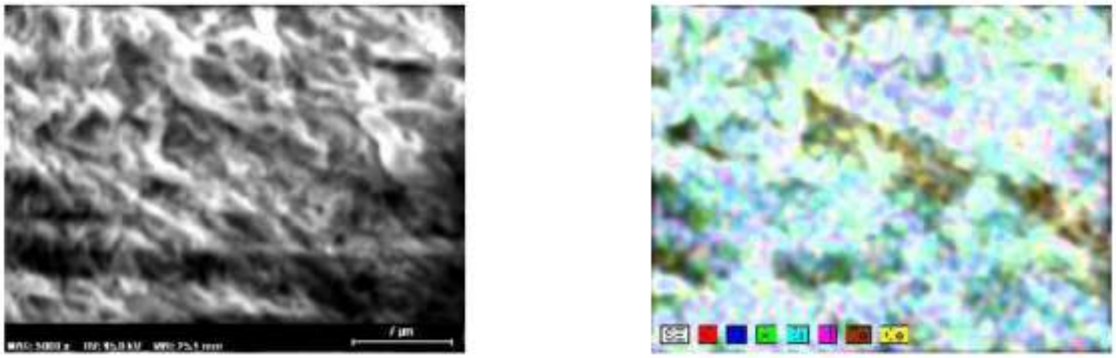
N-KA

Fe-KA

Ce-LA

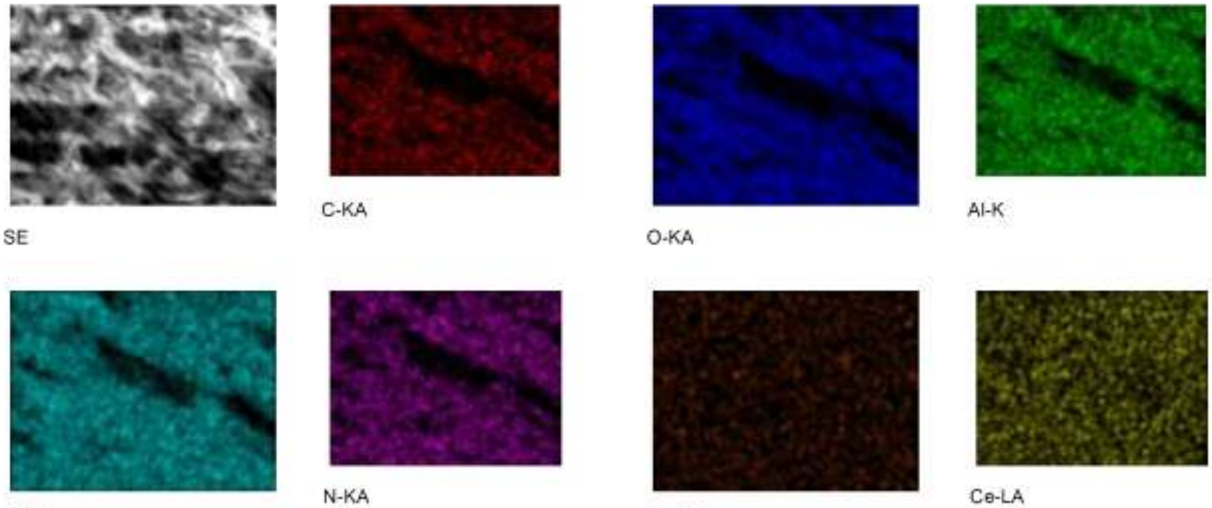
Fig. S3 EDX- SEM (×300) from **1** on montmorillonite.





SEM image

Map data



SE

C-KA

O-KA

Al-K

Si-K

N-KA

Fe-KA

Ce-LA

Fig. S4 EDX- SEM (×5000) from **1** on montmorillonite (100 mg) after reaction with Ce(IV) (40 mL, 0.11 M).

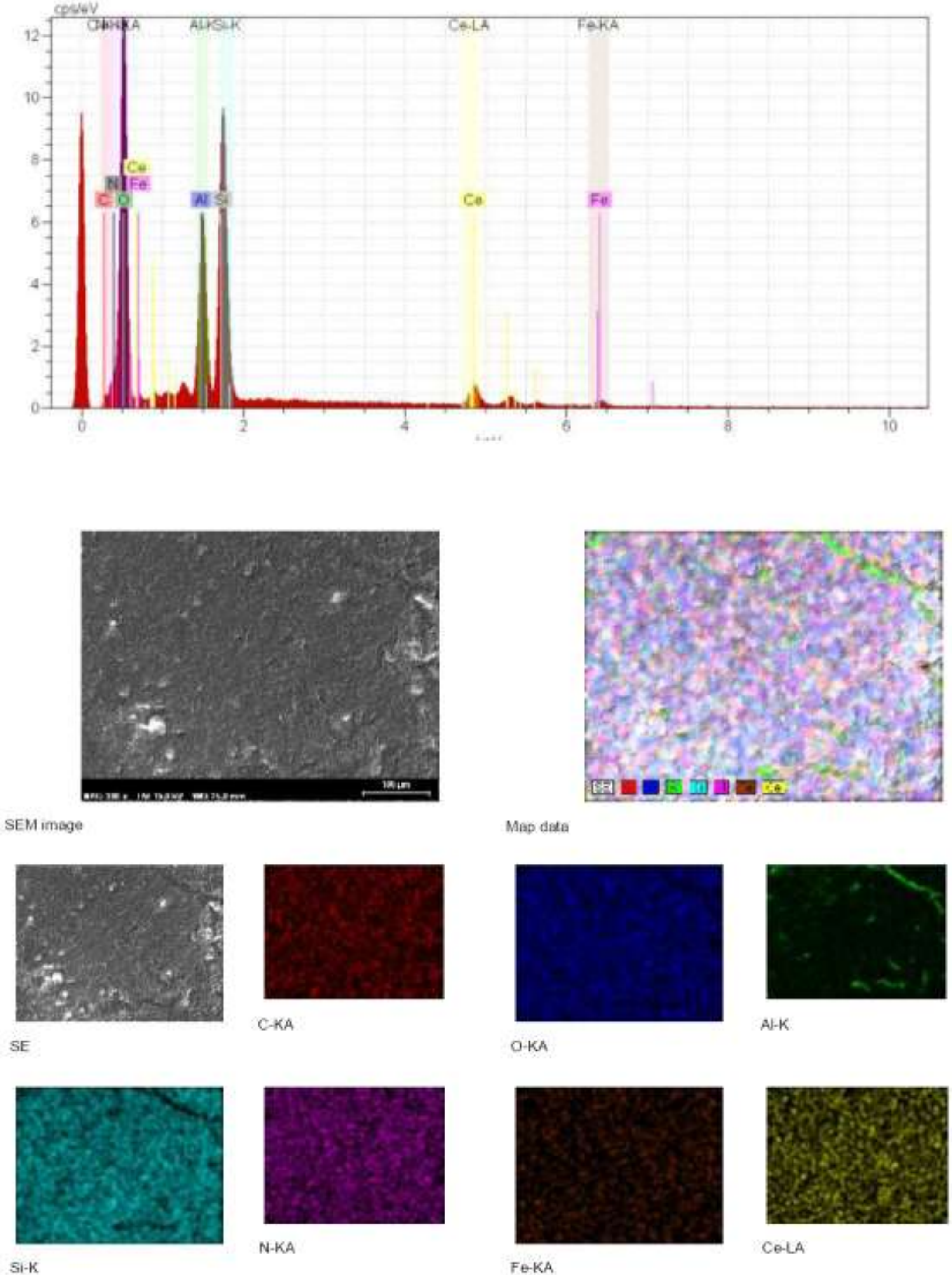


Fig. S5 EDX- SEM (×300) from **1** on montmorillonite (100 mg) after reaction with Ce(IV) (40 mL, 0.11 M).

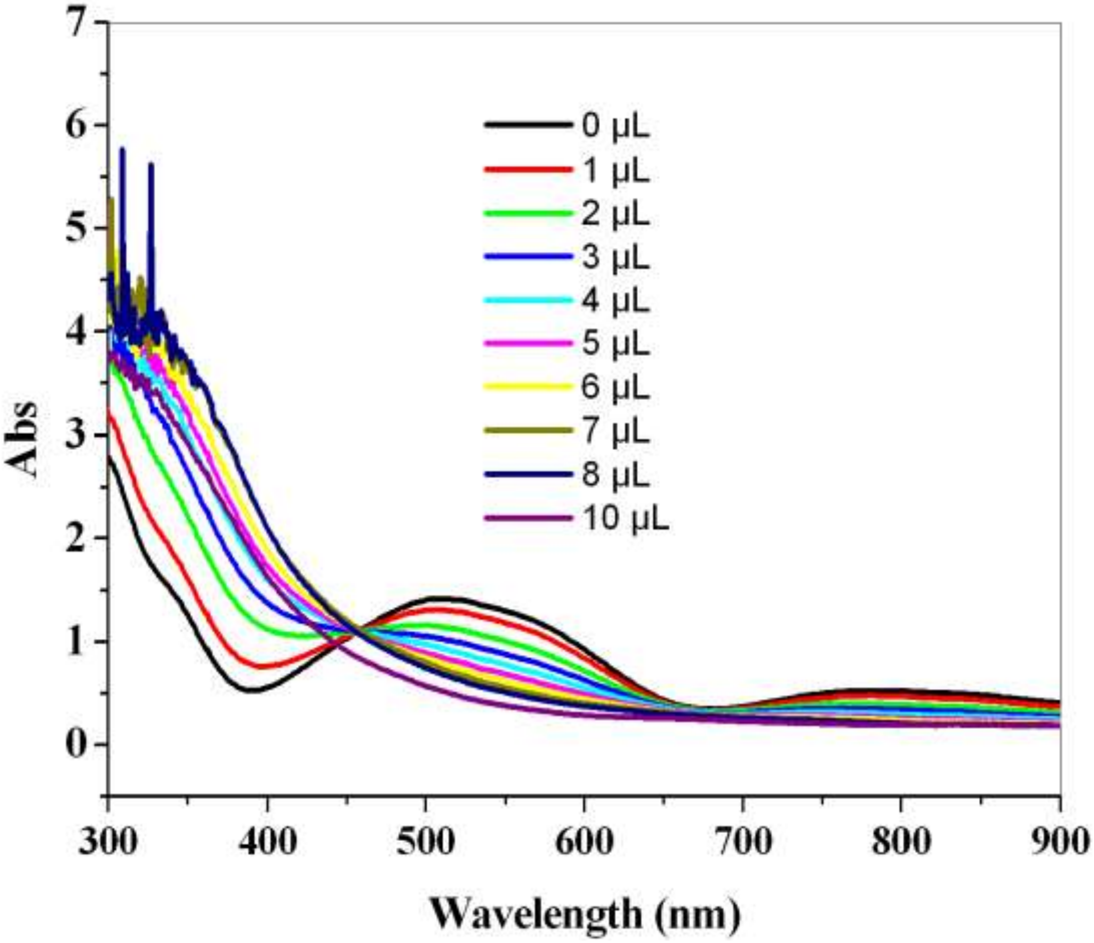
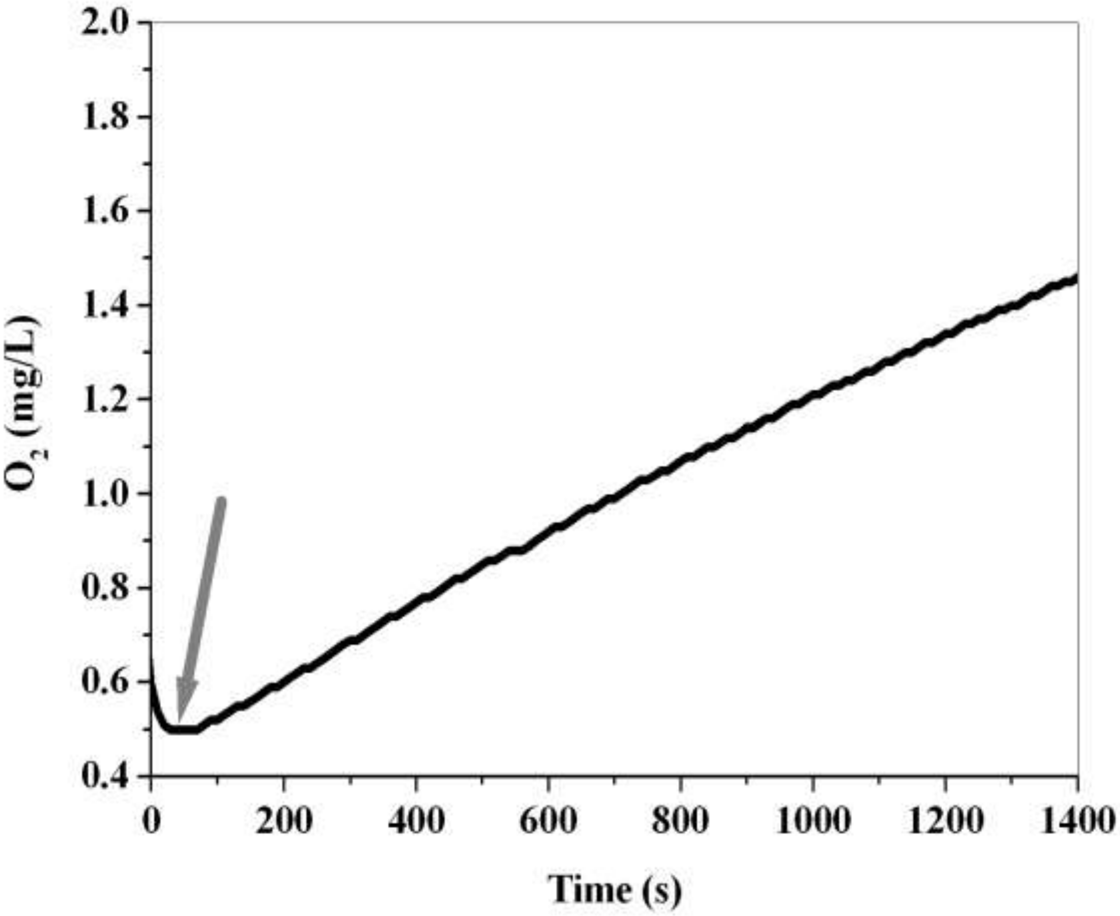
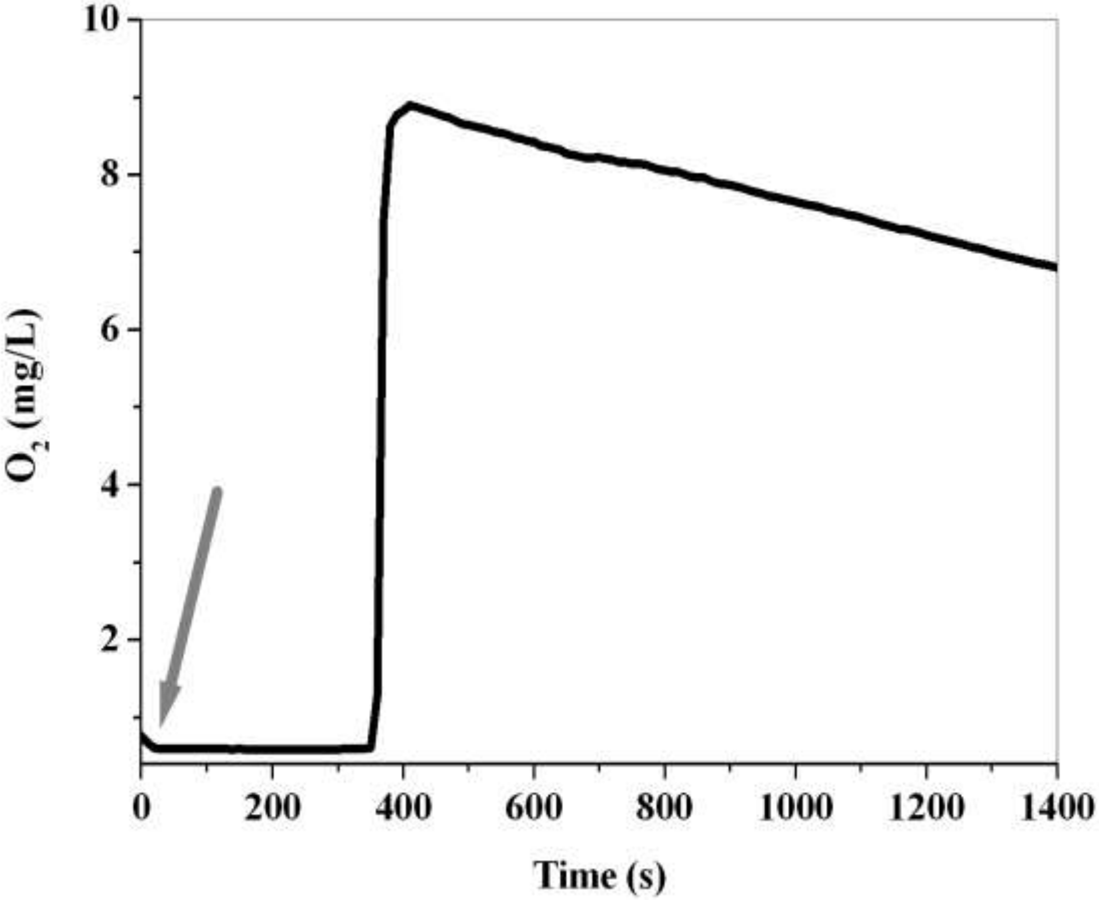


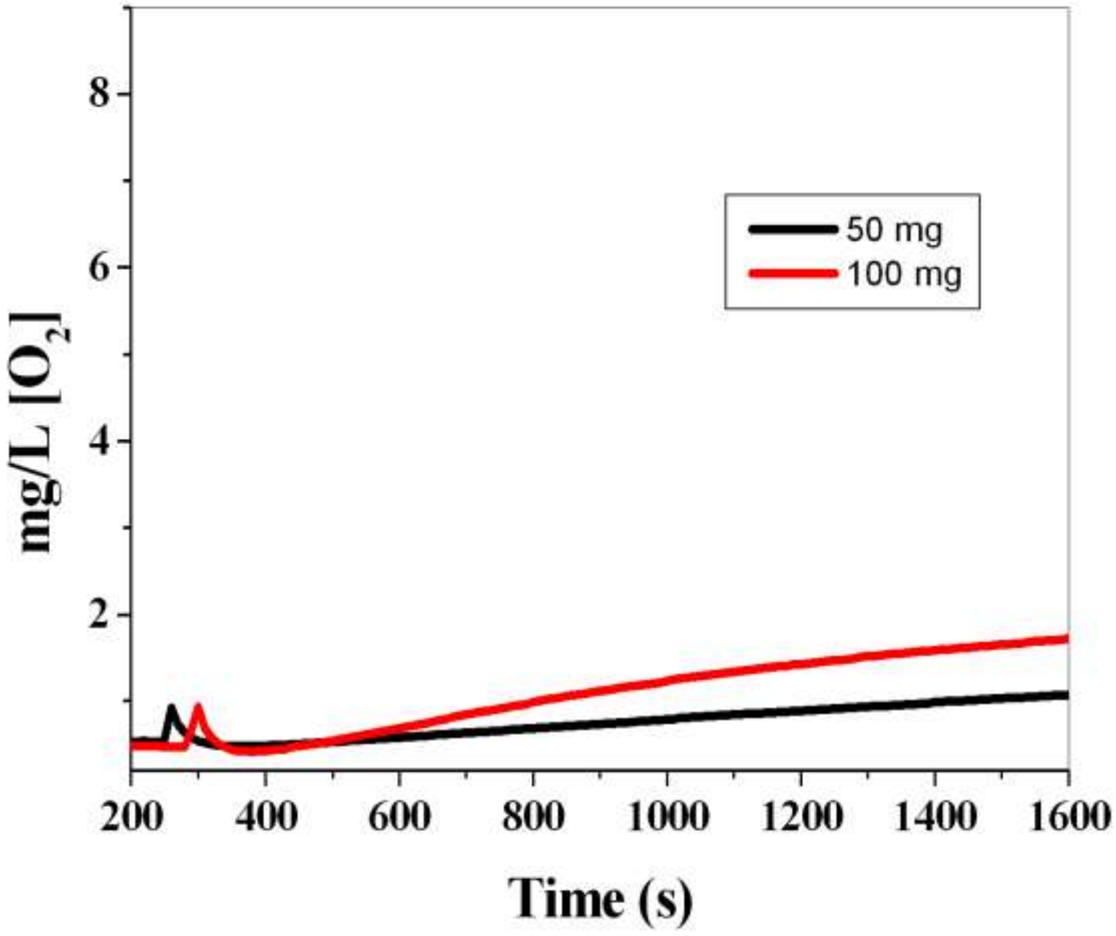
Fig. S6 UV-VIS spectra of the mixture of K_2FeO_4 (0.6 mg, 3 mL) and 1-10 µL Ce(IV) (0.1M).


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
O_2 (mg/L)
0
200
400
600
800
1000
1200
1400
Time (s)

a



b



c

Fig. S7 Oxygen evolution in the reaction of K_2FeO_4 (1.25 mM) with water (40 mL, pH ~6) at 25 °C. The arrow shows the time at which K_2FeO_4 was added to the Ce(IV) solution (a). Oxygen evolution in the reaction of K_2FeO_4 (0.5 mM) with water (40 mL, pH ~ 1 (HNO_3)) at 25 °C. The arrow shows the time at which K_2FeO_4 was added to the Ce(IV) solution (b). Low O_2 evolution is observed for **1** on montmorillonite (50 or 100 mg) in the presence of Ce(IV) (40 mL, 0.11 M). The content of Fe is 1% in this compound (c).

Tables

Table S1. Selected X-ray data for **1**.

	1
Formula	$C_{36}H_{40}Fe_2N_8O_3 \cdot 4(ClO_4) \cdot 4(H_2O)$
Formula weight	1214.32
Temperature [K]	100(2)
λ [Å]	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	11.754 (3)
b [Å]	28.117 (4)
c [Å]	30.475 (5)
α [°]	84.09 (3)
β [°]	84.78 (3)
γ [°]	87.29 (3)
V [$Å^3$]	9969 (3)
Z, ρ_{calc} [g cm^{-3}]	8, 1.618
μ [mm^{-1}]	0.89
F(000)	4992
Crystal size [mm]	0.31 × 0.24 × 0.15
θ range[º]	1.35-26.77
rflns: total/unique	133881/42087
R(int)	0.106
Abs. corr.	numerical
Min., max. transmission factors	0.792, 0.907
Data/restraints/params	42087/48/2674
GOF on F^2	0.61
R1 [$I > 2\sigma(I)$]	0.040
wR_2 (all data)	0.071
Max., min. $\Delta\rho_{elect}$ [e $Å^{-3}$]	0.56, -0.52

Table S2. Selected geometric parameters [Å, °] for **1**.

Fe1—O1	1.801 (3)	Fe5—O7	1.802 (3)
Fe1—O2	2.055 (3)	Fe5—O8	2.052 (3)
Fe1—N3	2.127 (4)	Fe5—N19	2.108 (4)
Fe1—N1	2.142 (3)	Fe5—N17	2.129 (4)
Fe1—N2	2.154 (4)	Fe5—N18	2.143 (4)
Fe1—N4	2.247 (4)	Fe5—N20	2.242 (4)
Fe2—O1	1.797 (3)	Fe6—O7	1.782 (3)
Fe2—O3	2.052 (3)	Fe6—O9	2.086 (3)
Fe2—N6	2.113 (4)	Fe6—N21	2.108 (4)
Fe2—N5	2.118 (4)	Fe6—N23	2.120 (4)
Fe2—N7	2.122 (4)	Fe6—N22	2.140 (4)
Fe2—N8	2.261 (4)	Fe6—N24	2.259 (4)
Fe3—O4	1.795 (3)	Fe7—O10	1.776 (3)
Fe3—O5	2.077 (3)	Fe7—O11	2.071 (3)
Fe3—N11	2.111 (4)	Fe7—N26	2.115 (4)
Fe3—N9	2.118 (4)	Fe7—N27	2.131 (4)
Fe3—N10	2.120 (4)	Fe7—N25	2.143 (4)
Fe3—N12	2.252 (4)	Fe7—N28	2.246 (4)
Fe4—O4	1.795 (3)	Fe8—O10	1.795 (3)
Fe4—O6	2.068 (3)	Fe8—O12	2.095 (3)
Fe4—N14	2.122 (3)	Fe8—N31	2.104 (3)
Fe4—N15	2.128 (3)	Fe8—N30	2.132 (3)
Fe4—N13	2.156 (4)	Fe8—N29	2.140 (4)
Fe4—N16	2.229 (3)	Fe8—N32	2.234 (3)
O1—Fe1—O2	99.57 (14)	O7—Fe5—O8	100.45 (14)
O1—Fe1—N3	101.15 (14)	O7—Fe5—N19	97.97 (14)
O2—Fe1—N3	87.95 (13)	O8—Fe5—N19	90.36 (13)
O1—Fe1—N1	107.08 (14)	O7—Fe5—N17	108.72 (14)
O2—Fe1—N1	83.52 (13)	O8—Fe5—N17	83.79 (13)
N3—Fe1—N1	151.48 (13)	N19—Fe5—N17	153.28 (13)
O1—Fe1—N2	94.95 (14)	O7—Fe5—N18	96.73 (14)
O2—Fe1—N2	162.71 (12)	O8—Fe5—N18	160.06 (12)
N3—Fe1—N2	98.45 (15)	N19—Fe5—N18	97.23 (14)
N1—Fe1—N2	83.27 (14)	N17—Fe5—N18	81.17 (14)
O1—Fe1—N4	170.56 (15)	O7—Fe5—N20	170.95 (13)
O2—Fe1—N4	88.81 (13)	O8—Fe5—N20	86.11 (13)
N3—Fe1—N4	74.65 (14)	N19—Fe5—N20	75.61 (13)
N1—Fe1—N4	77.99 (13)	N17—Fe5—N20	78.00 (13)
N2—Fe1—N4	77.55 (14)	N18—Fe5—N20	78.04 (14)
O1—Fe2—O3	100.19 (13)	O7—Fe6—O9	98.11 (13)
O1—Fe2—N6	103.32 (15)	O7—Fe6—N21	104.81 (14)
O3—Fe2—N6	86.69 (13)	O9—Fe6—N21	85.13 (13)
O1—Fe2—N5	96.15 (14)	O7—Fe6—N23	101.81 (15)
O3—Fe2—N5	162.15 (14)	O9—Fe6—N23	87.22 (12)
N6—Fe2—N5	96.54 (14)	N21—Fe6—N23	153.08 (14)
O1—Fe2—N7	104.34 (15)	O7—Fe6—N22	99.86 (14)

O3—Fe2—N7	87.21 (14)	O9—Fe6—N22	159.74 (14)
N6—Fe2—N7	152.31 (14)	N21—Fe6—N22	81.31 (14)
N5—Fe2—N7	81.80 (15)	N23—Fe6—N22	98.14 (14)
O1—Fe2—N8	173.88 (14)	O7—Fe6—N24	177.03 (14)
O3—Fe2—N8	85.85 (13)	O9—Fe6—N24	84.11 (12)
N6—Fe2—N8	75.86 (14)	N21—Fe6—N24	77.29 (14)
N5—Fe2—N8	77.99 (13)	N23—Fe6—N24	76.27 (14)
N7—Fe2—N8	76.78 (14)	N22—Fe6—N24	78.28 (14)
Fe2—O1—Fe1	172.5 (2)	Fe6—O7—Fe5	168.71 (18)
O4—Fe3—O5	99.75 (13)	O10—Fe7—O11	99.44 (13)
O4—Fe3—N11	105.84 (14)	O10—Fe7—N26	100.94 (14)
O5—Fe3—N11	86.98 (14)	O11—Fe7—N26	85.44 (13)
O4—Fe3—N9	101.63 (14)	O10—Fe7—N27	104.75 (14)
O5—Fe3—N9	86.74 (13)	O11—Fe7—N27	84.77 (14)
N11—Fe3—N9	152.47 (14)	N26—Fe7—N27	153.67 (14)
O4—Fe3—N10	97.10 (14)	O10—Fe7—N25	97.22 (14)
O5—Fe3—N10	161.56 (14)	O11—Fe7—N25	160.25 (14)
N11—Fe3—N10	81.24 (14)	N26—Fe7—N25	101.75 (14)
N9—Fe3—N10	97.18 (14)	N27—Fe7—N25	80.79 (15)
O4—Fe3—N12	174.08 (14)	O10—Fe7—N28	173.75 (14)
O5—Fe3—N12	85.42 (13)	O11—Fe7—N28	86.12 (13)
N11—Fe3—N12	77.15 (14)	N26—Fe7—N28	76.52 (15)
N9—Fe3—N12	75.65 (14)	N27—Fe7—N28	78.47 (14)
N10—Fe3—N12	78.18 (14)	N25—Fe7—N28	77.88 (15)
O4—Fe4—O6	99.87 (13)	O10—Fe8—O12	98.23 (13)
O4—Fe4—N14	106.21 (14)	O10—Fe8—N31	100.21 (13)
O6—Fe4—N14	82.01 (13)	O12—Fe8—N31	86.60 (13)
O4—Fe4—N15	100.63 (14)	O10—Fe8—N30	105.16 (14)
O6—Fe4—N15	85.21 (13)	O12—Fe8—N30	83.99 (12)
N14—Fe4—N15	151.85 (13)	N31—Fe8—N30	153.93 (13)
O4—Fe4—N13	95.27 (14)	O10—Fe8—N29	97.24 (13)
O6—Fe4—N13	162.51 (12)	O12—Fe8—N29	161.23 (12)
N14—Fe4—N13	85.41 (13)	N31—Fe8—N29	101.05 (14)
N15—Fe4—N13	100.61 (14)	N30—Fe8—N29	81.76 (13)
O4—Fe4—N16	169.98 (14)	O10—Fe8—N32	173.54 (13)
O6—Fe4—N16	89.14 (12)	O12—Fe8—N32	87.02 (12)
N14—Fe4—N16	79.23 (13)	N31—Fe8—N32	76.24 (13)
N15—Fe4—N16	75.59 (13)	N30—Fe8—N32	79.03 (13)
N13—Fe4—N16	76.56 (13)	N29—Fe8—N32	78.34 (13)
Fe4—O4—Fe3	174.81 (19)	Fe7—O10—Fe8	174.16 (18)

Table S3. Selected hydrogen bonding parameters [Å, °] for **1**. Symmetry codes: (i) -x, -y+1, -z; (ii) x-1, y, z; (iii) x+1, y, z; (iv) -x+1, -y+1, -z+1; (v) -x+1, -y+1, -z.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1W2···O79	1.02	1.61	2.627 (4)	175
O2—H2W2···O78	0.82	1.82	2.634 (4)	169
O3—H1W3···O82	0.82	1.86	2.612 (4)	153
O3—H2W3···O83	0.82	1.86	2.649 (5)	162
O5—H1W5···O87$^{\mathrm{i}}$	0.82	1.89	2.681 (4)	162
O6—H1W6···O80$^{\mathrm{ii}}$	0.82	1.87	2.688 (4)	175
O8—H1W8···O88$^{\mathrm{iii}}$	0.82	1.84	2.658 (4)	176
O2—H1W2···O79	1.02	1.61	2.627 (4)	175
O2—H2W2···O78	0.82	1.82	2.634 (4)	169
O3—H1W3···O82	0.82	1.86	2.612 (4)	153
O3—H2W3···O83	0.82	1.86	2.649 (5)	162
O5—H1W5···O87$^{\mathrm{i}}$	0.82	1.89	2.681 (4)	162
O6—H1W6···O80$^{\mathrm{ii}}$	0.82	1.87	2.688 (4)	175
O8—H1W8···O88$^{\mathrm{iii}}$	0.82	1.84	2.658 (4)	176
O9—H1W9···O85$^{\mathrm{iii}}$	0.82	1.89	2.704 (4)	176
O11—H111···O89	0.82	1.80	2.599 (7)	164
O11—H111···O891	0.82	1.88	2.619 (7)	149
O12—H112···O81	0.82	1.83	2.641 (4)	172
O77—H177···O69$^{\mathrm{ii}}$	0.82	1.92	2.74 (3)	173
O77—H177···O691$^{\mathrm{ii}}$	0.82	2.12	2.94 (2)	179
O77—H277···O18	0.82	2.26	2.990 (5)	149
O77—H277···O19	0.82	2.64	3.296 (6)	139
O78—H178···O31$^{\mathrm{iv}}$	0.82	2.11	2.894 (4)	160
O78—H278···O41$^{\mathrm{iv}}$	0.82	2.06	2.872 (5)	169
O78—H278···Cl8$^{\mathrm{iv}}$	0.82	2.91	3.698 (4)	163
O79—H179···O2W	0.82	2.09	2.894 (6)	168
O80—H180···O13$^{\mathrm{iii}}$	0.82	2.21	2.823 (6)	132
O81—H181···O22$^{\mathrm{v}}$	0.82	2.05	2.815 (5)	154
O82—H182···O57	0.82	2.06	2.832 (5)	156
O83—H183···O28	0.82	2.10	2.834 (4)	149
O83—H283···O59	0.82	2.10	2.910 (4)	170
O84—H184···O53	0.82	2.02	2.829 (5)	167
O86—H186···O37	0.82	2.04	2.794 (4)	153
O86—H186···Cl7	0.82	2.97	3.605 (3)	136
O86—H286···O14	0.82	2.06	2.868 (5)	166
O86—H286···Cl1	0.82	2.88	3.683 (4)	166
O88—H881···O1W	0.82	1.93	2.729 (4)	166

References

1 B. R. Whittlesey, Z. Pang, R. A. Holwerda, Inorg. Chim. Acta, 1999, **284**, 124.
2 G. M. Sheldrick, SHELXTL 5.1, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA, 1997.
3 A. Hazell, K. B. Jensen, C. J. McKenzie, H. Toftlund, *Inorg. Chem.*, 1994, **33**, 3127.