Electronic Supplementary Information

Hybrid compound based on diethylenetriaminecopper(II) cations and scarce V-monosubstituted β-octamolybdate as water oxidation catalyst

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Crystallography details

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_8H_{41}Cu_2Mo_7N_7O_{31.5}V$
Formula weight	1589.08
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8374(5)
b/Å	13.8773(7)
c/Å	14.1652(8)
α/°	90
β/°	93.260(5)
γ/°	90
Volume/Å^3	1930.65(17)
Z	2
ρ_{calc}g/cm^3	2.734
μ/mm^{-1}	3.609
F(000)	1530.0
Crystal size/mm^3	0.6 × 0.5 × 0.4
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.466 to 64.96
Index ranges	$-14 \leq h \leq 13$, $-19 \leq k \leq 18$, $-12 \leq l \leq 21$
Reflections collected	12738
Independent reflections	6128 [R_{int} = 0.0414, R_{sigma} = 0.0623]
Data/restraints/parameters	6128/0/259
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0573, wR_2 = 0.1405
Final R indexes [all data]	R_1 = 0.0879, wR_2 = 0.1721
Largest diff. peak/hole / e Å^{-3}	1.98/-2.02

Table S2. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

Atom	***x***	***y***	***z***	**U(eq)**
Mo1	1170.9(7)	-279.1(5)	974.3(5)	30.48(17)
Mo2	1482.2(6)	-1411.7(4)	-976.2(4)	34.43(15)
Mo3	1816.0(6)	636.4(4)	-2045.3(5)	38.89(16)
Mo4	1490.9(6)	1735.1(4)	-62.8(4)	34.15(15)
V1	1170.9(7)	-279.1(5)	974.3(5)	30.48(17)
O1	851(5)	-1503(3)	328(3)	33.5(10)
O2	492(5)	-598(3)	2025(4)	38.8(10)
O3	840(5)	1083(3)	1068(3)	34.4(9)
O4	2828(5)	-318(4)	1230(4)	41.8(11)
O5	1070(5)	-2525(4)	-1401(4)	46.5(12)
O6	1447(5)	-717(4)	-2136(4)	40.7(11)
O7	3200(5)	-1459(4)	-685(4)	43.6(12)
O8	3530(6)	572(4)	-1762(4)	49.3(13)
O9	1694(7)	953(4)	-3213(4)	56.9(14)
O10	1446(5)	1808(3)	-1405(4)	40.5(11)
O11	3196(5)	1639(4)	214(4)	44.7(12)
O12	1119(6)	2916(3)	190(4)	49.0(13)
O13	1197(5)	167(3)	-490(3)	34.4(10)
N1S	5000	0	0	41.1(19)
Cu1	2687.5(12)	689.5(7)	3664.4(9)	56.3(3)
O1S	2219(10)	-659(5)	3943(7)	97(3)
O2S	3548(7)	820(4)	5234(5)	63.9(17)
N1	4486(9)	309(6)	3187(6)	66(2)
N2	3167(10)	1995(5)	3202(6)	68(2)
N3	813(10)	1208(7)	3667(7)	79(3)
C1	5236(12)	1167(8)	2907(8)	73(3)
C2	4206(13)	1870(7)	2526(7)	74(3)
C3	1928(13)	2468(7)	2818(8)	75(3)
C4	876(12)	2271(7)	3495(8)	74(3)
O3S	-168(9)	1636(6)	5549(6)	66(2)

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Mo1	26.1(3)	27.0(3)	38.3(4)	1.9(3)	1.3(3)	0.5(2)
Mo2	29.6(3)	30.2(3)	43.8(3)	-0.7(2)	5.4(2)	2.1(2)
Mo3	36.2(3)	37.2(3)	44.3(4)	1.7(2)	11.1(2)	-3.1(2)
Mo4	30.1(3)	27.3(3)	45.4(3)	0.0(2)	4.6(2)	-3.32(19)
V1	26.1(3)	27.0(3)	38.3(4)	1.9(3)	1.3(3)	0.5(2)
O1	35(2)	25(2)	41(3)	3.8(18)	1.5(19)	-2.5(16)
O2	36(3)	40(3)	41(3)	1(2)	6(2)	-1.9(19)
O3	31(2)	33(2)	39(2)	-1.4(19)	5.4(18)	-3.3(18)
O4	34(3)	42(3)	50(3)	4(2)	5(2)	3(2)
O5	41(3)	36(3)	63(3)	-6(2)	7(2)	1(2)
O6	35(3)	44(3)	44(3)	-2(2)	10(2)	5(2)
O7	32(2)	50(3)	50(3)	1(2)	10(2)	3(2)
O8	39(3)	48(3)	61(4)	-5(3)	14(2)	-5(2)
O9	64(4)	59(3)	50(3)	3(3)	15(3)	-4(3)
O10	39(3)	35(2)	47(3)	4(2)	6(2)	-2.0(19)
O11	38(3)	44(3)	52(3)	0(2)	3(2)	-7(2)
O12	51(3)	28(2)	69(4)	-3(2)	12(3)	-2(2)
O13	33(2)	33(2)	39(3)	0.5(19)	5.4(18)	0.1(17)
N1S	16(3)	44(4)	64(6)	-1(4)	6(3)	-1(3)
Cu1	61.1(7)	42.0(5)	65.3(7)	-2.9(5)	-1.7(5)	-0.9(4)
O1S	110(7)	49(4)	131(8)	-1(4)	2(6)	-15(4)
O2S	68(4)	59(4)	66(4)	-10(3)	18(3)	0(3)
N1	73(6)	61(4)	67(5)	-3(4)	23(4)	4(4)
N2	98(7)	41(4)	61(5)	-5(3)	-27(5)	-5(4)
N3	88(7)	77(6)	71(6)	-2(5)	-9(5)	-6(5)
C1	86(8)	66(6)	67(6)	-10(5)	13(5)	-15(5)
C2	117(10)	55(5)	53(6)	-5(4)	25(6)	-33(6)
C3	109(9)	47(5)	65(6)	-4(4)	-22(6)	-8(5)
C4	89(8)	57(5)	73(7)	-18(5)	-34(6)	22(5)
O3S	73(6)	54(5)	72(6)	6(4)	9(5)	5(4)

Table S4. Bond lengths (Å) for **1**.

Mo1	Mo2	3.2084(10)		Mo4	O10	1.902(5)
Mo1	Mo4	3.1817(9)		Mo4	O11	1.706(5)
Mo1	O1	1.946(4)		Mo4	O12	1.721(5)
Mo1	O2	1.723(5)		Mo4	O13	2.273(4)
Mo1	O3	1.924(5)		V1	O1	1.946(4)
Mo1	O4	1.650(5)		V1	O2	1.723(5)
Mo1	O13[1]	2.396(5)		V1	O3	1.924(5)
Mo1	O13	2.166(5)		V1	O4	1.650(5)
Mo2	O1	1.985(5)		V1	O13	2.166(5)
Mo2	O3[1]	2.326(5)		V1	O13[1]	2.396(5)
Mo2	O5	1.698(5)		Cu1	O1S	1.972(7)
Mo2	O6	1.904(5)		Cu1	O2S	2.341(7)
Mo2	O7	1.718(5)		Cu1	N1	2.001(8)
Mo2	O13	2.318(4)		Cu1	N2	1.993(8)
Mo3	O2[1]	2.273(5)		Cu1	N3	1.979(10)
Mo3	O6	1.916(5)		N1	C1	1.467(13)
Mo3	O8	1.713(6)		N2	C2	1.449(14)
Mo3	O9	1.709(6)		N2	C3	1.462(13)
Mo3	O10	1.907(5)		N3	C4	1.496(13)
Mo3	O13	2.409(5)		C1	C2	1.486(16)
Mo4	O1[1]	2.336(4)		C3	C4	1.476(17)
Mo4	O3	1.977(5)				

[1]-X,-Y,-Z

Table S5. Bond angles (°) for **1**.

Mo4	Mo1	Mo2	90.92(2)		O10	Mo4	O3	147.54(19)
O1	Mo1	Mo2	35.72(14)		O10	Mo4	O13	77.86(19)
O1	Mo1	Mo4	124.52(14)		O11	Mo4	Mo1	86.96(18)
O1	Mo1	O13	78.99(18)		O11	Mo4	O1[1]	166.9(2)
O1	Mo1	O13[1]	78.08(17)		O11	Mo4	O3	97.9(2)
O2	Mo1	Mo2	132.73(16)		O11	Mo4	O10	101.6(2)
O2	Mo1	Mo4	132.66(16)		O11	Mo4	O12	104.2(3)
O2	Mo1	O1	97.0(2)		O11	Mo4	O13	95.4(2)
O2	Mo1	O3	96.8(2)		O12	Mo4	Mo1	135.5(2)
O2	Mo1	O13	157.9(2)		O12	Mo4	O1[1]	86.9(2)
O2	Mo1	O13[1]	81.1(2)		O12	Mo4	O3	100.7(2)
O3	Mo1	Mo2	124.42(14)		O12	Mo4	O10	99.4(3)
O3	Mo1	Mo4	35.91(14)		O12	Mo4	O13	160.3(2)
O3	Mo1	O1	150.0(2)		O13	Mo4	Mo1	42.88(12)
O3	Mo1	O13[1]	77.90(17)		O13	Mo4	O1[1]	73.47(16)

O3	Mo1	O13	78.24(18)		O1	V1	O13[1]	78.08(17)
O4	Mo1	Mo2	91.79(19)		O1	V1	O13	78.99(18)
O4	Mo1	Mo4	90.45(18)		O2	V1	O1	97.0(2)
O4	Mo1	O1	101.9(2)		O2	V1	O3	96.8(2)
O4	Mo1	O2	103.2(3)		O2	V1	O13[1]	81.1(2)
O4	Mo1	O3	100.7(2)		O2	V1	O13	157.9(2)
O4	Mo1	O13	98.9(2)		O3	V1	O1	150.0(2)
O4	Mo1	O13[1]	175.6(2)		O3	V1	O13	78.24(18)
O13	Mo1	Mo2	46.26(12)		O3	V1	O13[1]	77.90(17)
O13[1]	Mo1	Mo2	85.64(11)		O4	V1	O1	101.9(2)
O13	Mo1	Mo4	45.57(12)		O4	V1	O2	103.2(3)
O13[1]	Mo1	Mo4	86.03(11)		O4	V1	O3	100.7(2)
O13	Mo1	O13[1]	76.78(19)		O4	V1	O13	98.9(2)
O1	Mo2	Mo1	34.91(12)		O4	V1	O13[1]	175.6(2)
O1	Mo2	O3[1]	72.92(18)		O13	V1	O13[1]	76.78(19)
O1	Mo2	O13	74.58(17)		Mo1	O1	Mo2	109.4(2)
O3[1]	Mo2	Mo1	79.07(12)		Mo2	O1	Mo4[1]	102.53(19)
O5	Mo2	Mo1	135.9(2)		V1	O1	Mo2	109.4(2)
O5	Mo2	O1	101.0(2)		Mo1	O3	Mo4	109.3(2)
O5	Mo2	O3[1]	86.8(2)		Mo4	O3	Mo2[1]	103.15(19)
O5	Mo2	O6	99.4(3)		V1	O3	Mo4	109.3(2)
O5	Mo2	O7	105.2(3)		Mo2	O6	Mo3	116.4(3)
O5	Mo2	O13	159.1(2)		Mo4	O10	Mo3	115.8(2)
O6	Mo2	Mo1	119.83(15)		Mo1	O13	Mo2	91.30(16)
O6	Mo2	O1	147.55(19)		Mo1	O13	Mo3	166.0(2)
O6	Mo2	O3[1]	83.30(19)		Mo1[1]	O13	Mo3	90.72(16)
O6	Mo2	O13	77.39(19)		Mo1	O13	Mo4	91.56(17)
O7	Mo2	Mo1	87.29(18)		Mo2	O13	Mo1[1]	96.22(16)
O7	Mo2	O1	97.4(2)		Mo2	O13	Mo3	86.70(16)
O7	Mo2	O3[1]	166.1(2)		Mo4	O13	Mo1[1]	96.95(17)
O7	Mo2	O6	101.3(2)		Mo4	O13	Mo2	165.5(2)
O7	Mo2	O13	95.7(2)		Mo4	O13	Mo3	87.10(15)
O13	Mo2	Mo1	42.44(12)		V1	O13	Mo2	91.30(16)
O13	Mo2	O3[1]	72.32(16)		V1	O13	Mo3	166.0(2)
O2[1]	Mo3	O13	71.16(17)		V1	O13	Mo4	91.56(17)
O6	Mo3	O2[1]	78.02(19)		O1S	Cu1	O2S	87.7(3)
O6	Mo3	O13	74.92(19)		O1S	Cu1	N1	92.2(4)
O8	Mo3	O2[1]	165.1(2)		O1S	Cu1	N2	172.2(4)
O8	Mo3	O6	98.3(2)		O1S	Cu1	N3	96.7(4)
O8	Mo3	O10	98.4(2)		N1	Cu1	O2S	93.6(3)
O8	Mo3	O13	93.9(2)		N2	Cu1	O2S	99.4(3)
O9	Mo3	O2[1]	90.2(2)		N2	Cu1	N1	84.2(4)
O9	Mo3	O6	100.6(3)		N3	Cu1	O2S	104.9(3)
O9	Mo3	O8	104.7(3)		N3	Cu1	N1	159.8(4)
O9	Mo3	O10	103.7(3)		N3	Cu1	N2	84.7(4)

O9	Mo3	O13	161.3(2)		C1	N1	Cu1	110.2(7)
O10	Mo3	O2[1]	78.22(19)		C2	N2	Cu1	107.3(6)
O10	Mo3	O6	145.8(2)		C2	N2	C3	114.4(9)
O10	Mo3	O13	74.37(19)		C3	N2	Cu1	108.8(7)
O1[1]	Mo4	Mo1	80.22(11)		C4	N3	Cu1	108.1(7)
O3	Mo4	Mo1	34.81(13)		N1	C1	C2	106.7(9)
O3	Mo4	O1[1]	72.84(17)		N2	C2	C1	109.3(8)
O3	Mo4	O13	74.64(18)		N2	C3	C4	106.0(9)
O10	Mo4	Mo1	120.73(14)		C3	C4	N3	109.0(9)
O10	Mo4	O1[1]	83.11(19)					

[1]-X,-Y,-Z

Table S6. H atoms coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **1**.

Atom	***x***	***y***	***z***	**U(eq)**
H1SC	5624.4	-410.1	130.8	62
H1SD	4376.4	-59.5	387.2	62
H1SE	5331.6	565.7	43.3	62
H1SF	4669.6	-93.6	-558.9	62
H1SA	2874.53	-963.78	4269.4	146
H1SB	2147.83	-933.48	3406.6	146
H2SA	4432.46	985.67	5207.52	96
H2SB	3186.46	1315.57	5507.52	96
H1A	4971.62	-6.77	3637.06	79
H1B	4355.29	-82.86	2692.27	79
H2	3549.29	2374.39	3736.84	81
H3A	286.78	926.53	3215.69	95
H3B	463.19	1092.1	4221.47	95
H1C	5863.54	1003.23	2427.66	87
H1D	5751.37	1437.21	3448	87
H2A	4639.65	2483.42	2411.54	89
H2B	3793.91	1636.97	1930.82	89
H3C	1656.04	2210.11	2199.92	90
H3D	2072.46	3156.62	2759.7	90
H4A	-2.04	2500.02	3241	89
H4B	1096.26	2604.8	4085.53	89
H3SA	-411.9	2104.13	5866.96	99
H3SB	-879.3	1235.93	5553.26	99

Table S7. Atomic occupancy for **1**.

Atom	Mo1	V1	H1SC	H1SD	H1SE	H1SF	O3S	H3SA	H3SB
Occupacy	0.5	0.5	0.5	0.5	0.5	0.5	0.75	0.75	0.75

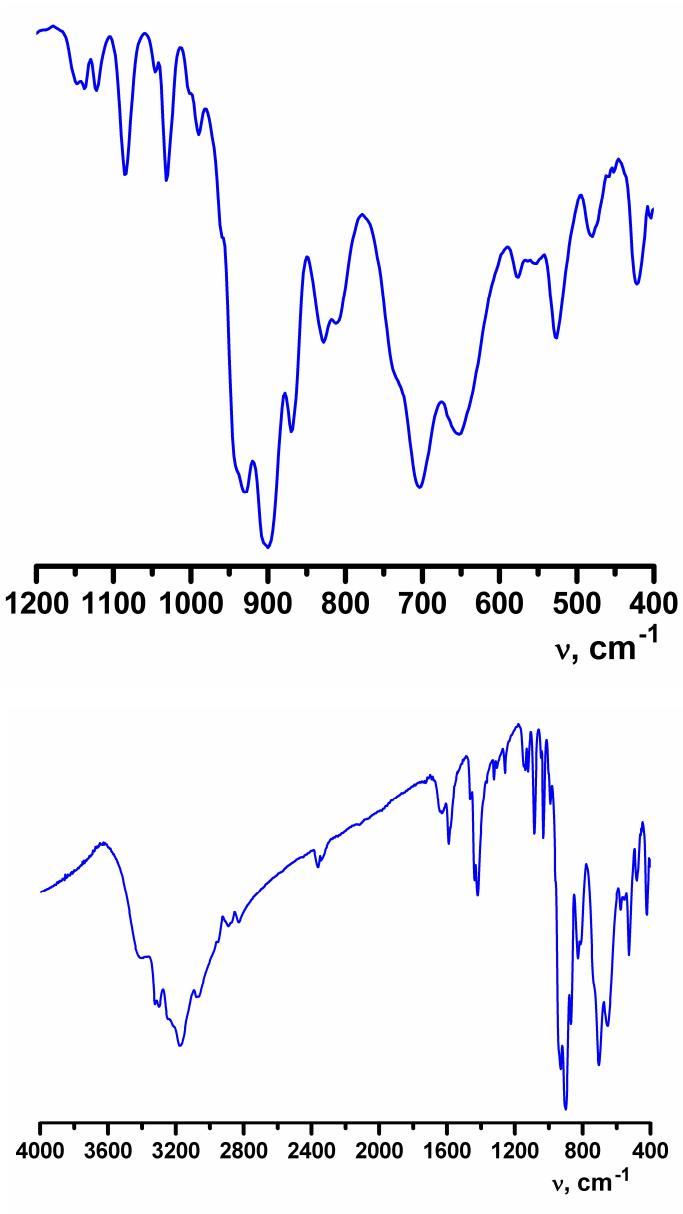

Figure S1. FTIR spectra of the title compound recorded in KBr pellets.

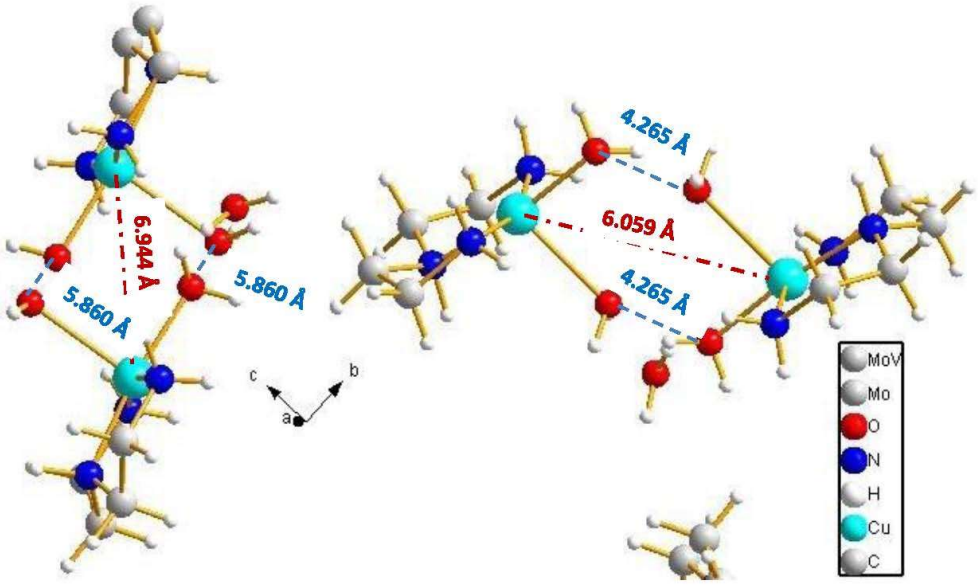

Figure S2. Fragment of the crystal structure of the title compound showing intermolecular contacts Cu−O···O−Cu as dashed blue lines responsible for the weak antiferromagnetic exchange.

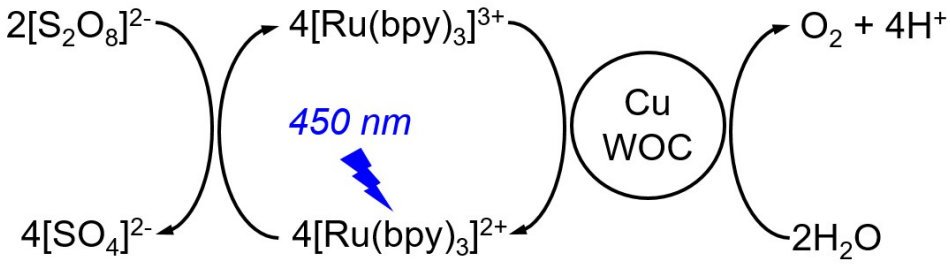

Figure S3. Scheme of the water oxidation catalysis using persulfate as electron acceptor, tris(bipyridine)ruthenium(II) as light harvester and the title compound as a water oxidation catalyst (WOC).

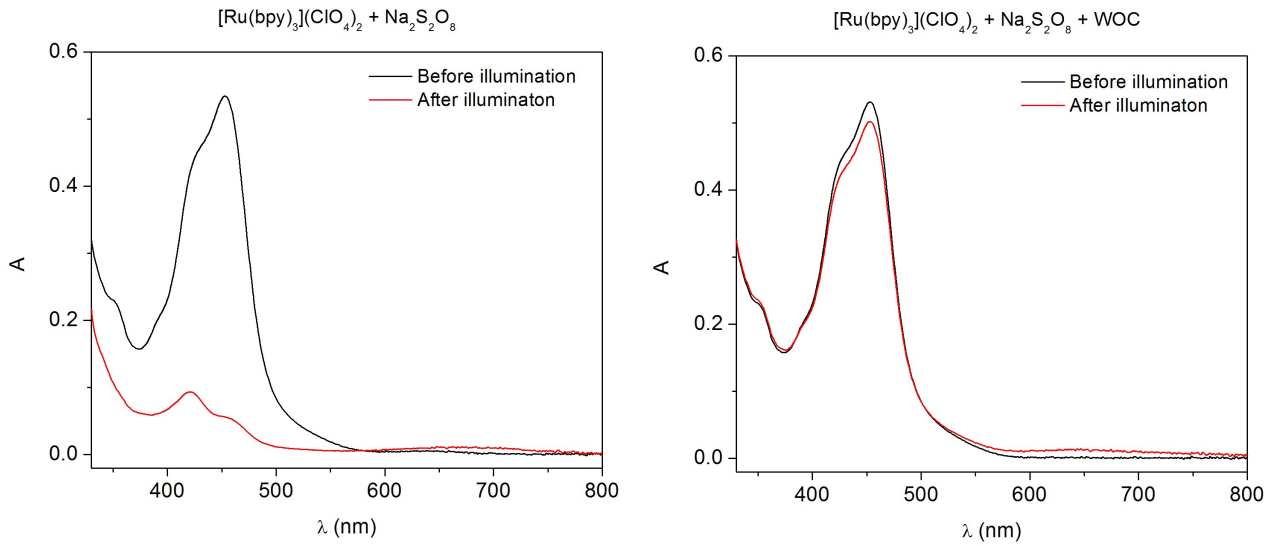

Figure S4. Left: steady-state UV-Vis absorption spectrum of the solution containing $[Ru(bpy)_3](ClO_4)_2$ (0.05 mM), $Na_2S_2O_8$ (1 mM) in borate buffer (pH 8.0) (black). After illumination of the cuvette at 450 nm during 10 s, the spectrum was recorded showing oxidation of Ru^{II} to Ru^{III} (red) as evidenced by the disappearance of the Ru^{II} band at λ_{max} = 453 nm. Right: the spectra of the solution containing $[Ru(bpy)_3](ClO_4)_2$ (0.05 mM), $Na_2S_2O_8$ (1 mM), and **1** (0.004 mM) in borate buffer (pH 8.0) before and after illumination. Accumulation of Ru^{III} is not observed.

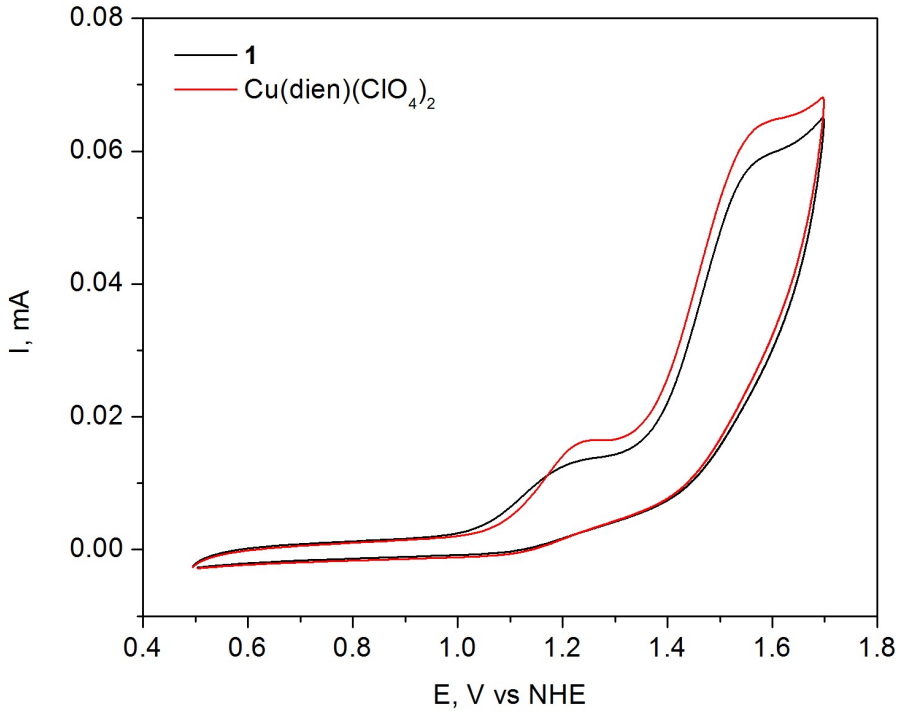

Figure S5. Cyclic voltammograms of **1** (black) and $Cu(dien)(ClO_4)_2$ (red), 0.25 mM, recorded at a scan rate of 100 mV s^{-1} in borate buffer (0.04 M, pH = 8.0) with supporting electrolyte $KClO_4$ (0.1 M).

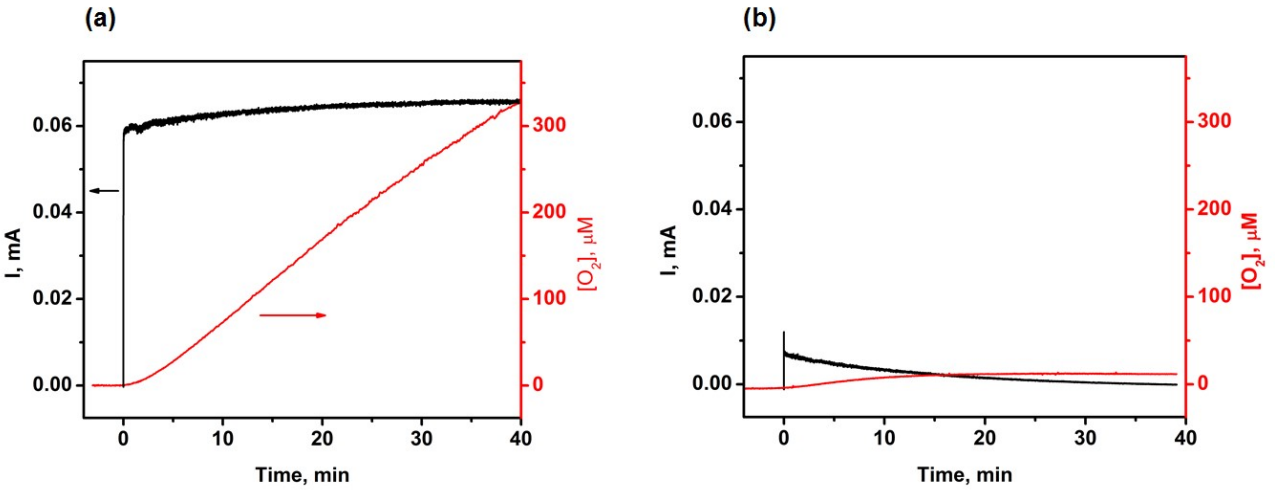

Figure S6. (**a**) Controlled potential electrolysis of the aqueous solution containing **1** (0.1 mM) and supporting electrolyte $KClO_4$ (0.1 M) in borate buffer (0.04 M, pH 8.0) with electric current shown in black and evolved oxygen in red. (**b**) Controlled potential electrolysis of the aqueous solution containing supporting electrolyte $KClO_4$ (0.1 M) in borate buffer (0.04 M, pH 8.0) only carried out using the working electrode transferred from the solution "**a**" after 45 min of electrolysis. The potential in all experiments was 1.55 V vs NHE.