SUPPORTING INFORMATION

A synthetic model for the oxygen-evolving complex in Sr^{2+}-containing photosystem II

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1. Experimental section

All manipulations were carried out under aerobic condition. Solvents were dried by using A4 molecule sieve. Other chemicals were used as received without further purification.

Synthesis of $Bu^n_4NMnO_4$: $Bu^n_4NMnO_4$ was prepared by mixing $KMnO_4$ (7.90g, 50mmol) and Bu^n_4NBr (17.73g, 55mmol) with vigorous stirring in 400 mL water solution. After 4 hours reaction, purple precipitate was collected by filtration, washed thoroughly with distilled water and diethyl ether, and dried in vacuum at ambient temperature. 16.93 g of final product was obtained, with yield of 93.7%. Elemental analysis (%) calculated: for $Bu^n_4NMnO_4$ ($C_{16}H_{36}NO_4Mn$): C, 53.17; H, 10.04; N, 3.88; found: C, 53.36; H, 9.95; N, 3.88.

Synthesis of complex 1: This complex was synthesized in a reaction of $Mn(CH_3CO_2)_2(H_2O)_4$ (0.368 g, 1.5 mmol), $Sr(CH_3CO_2)_2(H_2O)_{0.5}$ (0.322 g, 1.5 mmol), $Bu^n_4NMnO_4$ (2.168 g, 6 mmol) and pivalic acid (6.128 g, 60.0 mmol) in boiling acetonitrile (~100 mL). The final dark-brown solution was obtained in 25min. Precipitate was removed by filtration. Red-brown crystal (0.92 g, precursor of complex **1**) was formed at room temperature in four days. 0.588 g of precursor of complex **1** was dissolved into 9mL ethyl acetate in the presence of 2 % pyridine (v/v). The black rod crystal (0.184 g) of complex **1** was formed after several days at -20ºC, with a yield of 22 % (on Strontium basis). Elemental analysis (%) calcd. for complex **1** ($C_{70}H_{120}N_2O_{33}Mn_6Sr_2$): C, 41.57; H, 5.98; N, 1.38; found: C, 41.57; H, 5.79; N, 1.63.

EPR measurements: EPR spectra were recorded on a Bruker E500 spectrometer by using a standard resonance cavity (ST4102). The temperature (77K) was controlled by using a finger cryogenic dewar filled with liquid nitrogen. EPR conditions: Microwave frequency, 9.338 GHz; Microwave power, 10 mW; Modulation amplitude, 10 G; Modulation frequency, 100 kHz; Temperature, 77 K.

Electrochemical measurements: Electrochemical measurements were

performed using a three-electrode system connected to an Electrochemical Workstation (PGSTAT302N) from Metrohm Company. The working electrode was a glass carbon disc (diameter 3mm, freshly polished). The counter electrode was a platinum disc (diameter 3mm, freshly polished). The reference electrode was a $Ag/AgNO_3$ electrode (0.01 M $AgNO_3$, 0.1 M $^nBu_4NPF_6$ in acetonitrile). The electrolyte solution was 0.1M $Bu^n{}_4NPF_6$ in 3:2 ratio of 1, 2-dichiloroethane/ethyl acetate. Before the measurements, oxygen was removed from the solution by purging for 20-30 min with solvent-saturated argon. During the measurement, the solution was kept under argon. A background voltammogram of the electrolyte was recorded before dissolving the complex **1**. Reported potentials were referenced internally to NEH calibrated by the potential of ferrocene/ferrocenium measured under the same condition. Scan rate: 100mV/s. Arrows show the scan direction.

2. Crystal structure information

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

Empirical formula	$C_{70}H_{120}Mn_6N_2O_{33}Sr_2$
Formula weight	2022.56
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å	15.290(3)
b (Å)	18.205(4)
c (Å)	36.041(7)
α (º)	90.00
β (º)	90.00
γ (º)	90.00
V (Å^3)	10032(3)
Z	4
Calculated density (g/cm^3)	1.335
Temperature (K)	100(2)
θ range for data collection (º)	1.25 to 27.48
Absorption coefficient (mm^{-1})	1.854
Crystal size(mm^3)	0.15 × 0.11 × 0.05
Reflections collected	32066
Independent reflections	17540 [R_{int} = 0.0845]
Completeness to θ = 25.00 º	99.5%
Absorption correction	Semi-empirical from equivalents
Goodness-of-fit on F^2	1.078
Final R indices [$I > 2\ \theta\ (I)$]	$R1$ = 0.0813, $wR2$ = 0.2047
R indices (all data)	$R1$ = 0.0947, $wR2$ = 0.2202

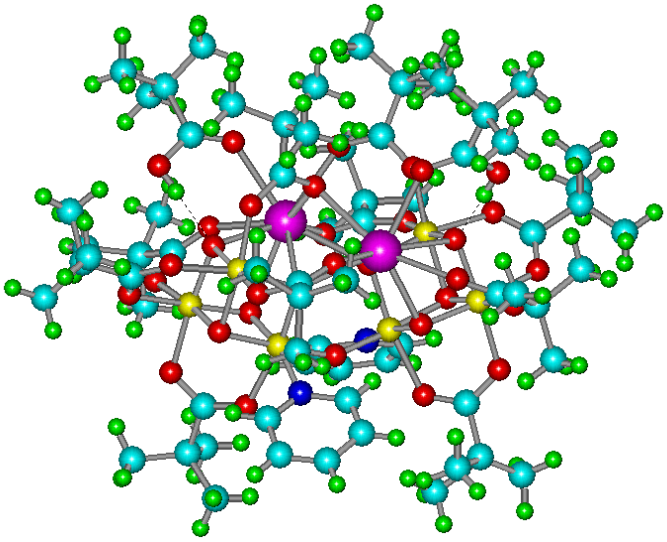

Fig. S1. The structure of complex **1**. Mn, Sr, O, N , C and H are shown in yellow, violet, red, blue, cyan and green, respectively.

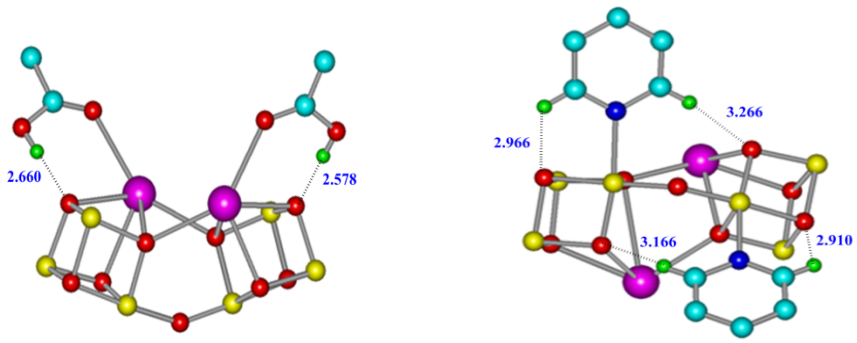

Fig. S2. H-bond interactions in the complex **1**. For clarity, only the core and the selected ligands are displayed. H-bonds are shown with dashed line, and values (Å) in blue color display the H-bond lengths of O…N, or, O…C. Mn, Sr, O, N, C and H are shown in yellow, violet, red, blue, cyan and green, respectively.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for complex **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	X	Y	Z	U(eq)
Sr(1)	2553(1)	9171(1)	8954(1)	26(1)
Sr(2)	4780(1)	10294(1)	8926(1)	23(1)
Mn(1)	4408(1)	11632(1)	9606(1)	22(1)
Mn(2)	3551(1)	10338(1)	9747(1)	22(1)
Mn(3)	2933(1)	11342(1)	9201(1)	21(1)
Mn(4)	2619(1)	10775(1)	8319(1)	23(1)
Mn(5)	3549(1)	9531(1)	8050(1)	25(1)
Mn(6)	1754(1)	9584(1)	8045(1)	25(1)
O(1)	5979(4)	9558(4)	9257(2)	32(2)
O(2)	6166(4)	10116(4)	9808(2)	28(1)
O(3)	5980(4)	11247(4)	9053(2)	31(2)
O(4)	5573(4)	11969(4)	9521(2)	29(1)
O(5)	4618(4)	11639(3)	10155(2)	26(1)
O(6)	3925(4)	10541(4)	10270(2)	26(1)
O(7)	4070(4)	9400(4)	9773(2)	30(1)
O(8)	3134(5)	8564(4)	9552(2)	35(2)
O(9)	4675(4)	10652(3)	9613(2)	24(1)
O(10)	3995(4)	12663(3)	9588(2)	26(1)
O(11)	3186(4)	10341(4)	9253(2)	29(1)
O(12)	3250(4)	11333(3)	9711(2)	24(1)
O(13)	4102(4)	11537(3)	9120(2)	25(1)
O(14)	2472(4)	10009(4)	9957(2)	29(1)
O(15)	1611(4)	9573(4)	9494(2)	31(1)
O(16)	2811(4)	12446(3)	9228(2)	26(1)
O(17)	2639(4)	11292(3)	8726(2)	23(1)
O(18)	1622(4)	11307(4)	8086(2)	31(1)
O(19)	937(4)	10320(4)	7839(2)	29(1)
O(20)	769(4)	9001(4)	8167(2)	34(2)
O(21)	1083(4)	8678(4)	8756(2)	32(2)
O(22)	1803(4)	10106(3)	8476(2)	26(1)
O(23)	2674(4)	10177(3)	7882(2)	28(1)
O(24)	2623(4)	8989(3)	8237(2)	29(1)
O(25)	3549(4)	10171(3)	8447(2)	25(1)
O(26)	1874(4)	9035(4)	7565(2)	31(1)
O(27)	3375(4)	8981(4)	7573(2)	30(1)
O(28)	2318(5)	7550(4)	8242(2)	42(2)
O(29)	2758(5)	7763(4)	8823(2)	40(2)
O(30)	4520(4)	10004(4)	7808(2)	29(1)
O(31)	5402(4)	10148(4)	8297(2)	33(2)

O(32)	4255(4)	8954(3)	8827(2)	27(1)
O(33)	4332(4)	8774(4)	8207(2)	29(1)
N(1)	1607(5)	11295(4)	9364(2)	25(2)
N(2)	3380(5)	11574(4)	8051(2)	28(2)
C(1)	6415(6)	9645(6)	9544(3)	33(2)
C(2)	7284(6)	9305(6)	9617(3)	35(2)
C(3)	7966(6)	9816(6)	9454(3)	39(2)
C(4)	7454(6)	9175(6)	10025(3)	37(2)
C(5)	7338(7)	8568(6)	9414(3)	45(2)
C(6)	3734(6)	8751(5)	9767(3)	29(2)
C(7)	4158(7)	8218(6)	10039(3)	36(2)
C(8)	3896(8)	7436(7)	9947(3)	48(3)
C(9)	5181(8)	8272(7)	10044(3)	47(3)
C(10)	3804(8)	8456(7)	10431(3)	50(3)
C(11)	6114(6)	11730(5)	9277(3)	28(2)
C(12)	6969(6)	12164(6)	9287(3)	33(2)
C(13)	7596(6)	11890(5)	8978(3)	35(2)
C(14)	7414(7)	12022(6)	9667(3)	36(2)
C(15)	6783(8)	12999(6)	9233(3)	46(3)
C(16)	4390(6)	11108(5)	10356(3)	28(2)
C(17)	4771(7)	11056(6)	10753(3)	40(2)
C(18)	4036(8)	10827(8)	11037(3)	57(3)
C(19)	5168(8)	11760(6)	10869(3)	47(3)
C(20)	5421(8)	10459(7)	10747(3)	47(3)
C(21)	3372(6)	12859(5)	9362(3)	28(2)
C(22)	3402(6)	13670(6)	9230(3)	40(2)
C(23)	4315(11)	13805(13)	9047(6)	56(4)
C(24)	3230(13)	14194(10)	9538(5)	45(3)
C(25)	2751(12)	13790(11)	8898(5)	51(3)
C(26)	1763(6)	9697(5)	9827(3)	28(2)
C(27)	1111(7)	9428(6)	10122(3)	40(2)
C(28)	180(7)	9545(7)	9984(4)	54(3)
C(29)	1279(8)	8575(8)	10138(4)	60(3)
C(30)	1277(9)	9746(9)	10500(4)	67(3)
C(31)	979(6)	11043(5)	9128(3)	28(2)
C(32)	121(6)	11095(6)	9223(3)	35(2)
C(33)	-121(6)	11414(5)	9556(3)	30(2)
C(34)	517(6)	11659(6)	9784(3)	32(2)
C(35)	1371(6)	11585(5)	9689(3)	29(2)
C(36)	996(7)	10986(6)	7927(3)	38(2)
C(37)	180(8)	11475(7)	7838(3)	54(2)
C(38)	481(9)	12273(8)	7769(4)	64(3)
C(39)	-383(10)	11493(9)	8176(4)	70(3)
C(40)	-324(10)	11164(9)	7512(4)	79(4)

C(41)	595(7)	8728(6)	8491(3)	36(2)
C(42)	-402(8)	8510(7)	8519(3)	49(2)
C(43)	-538(8)	8107(7)	8892(4)	55(3)
C(44)	-951(8)	9203(8)	8498(4)	60(3)
C(45)	-675(9)	8033(8)	8191(4)	61(3)
C(46)	2600(6)	8826(5)	7437(3)	32(2)
C(47)	2597(8)	8295(7)	7114(3)	53(2)
C(48)	1835(9)	8490(9)	6872(4)	69(3)
C(49)	2471(11)	7530(8)	7278(4)	78(4)
C(50)	3457(10)	8297(10)	6928(4)	80(4)
C(51)	2483(8)	7368(6)	8590(3)	41(2)
C(52)	2225(11)	6544(9)	8673(4)	70(3)
C(53)	2832(12)	6287(10)	8975(5)	93(4)
C(54)	2384(12)	6063(9)	8357(4)	89(4)
C(55)	1350(12)	6532(10)	8774(5)	98(4)
C(56)	4518(6)	8594(5)	8545(2)	24(2)
C(57)	5186(7)	7962(5)	8586(3)	33(2)
C(58)	5200(8)	7676(6)	8990(3)	46(2)
C(59)	6069(7)	8257(6)	8448(3)	39(2)
C(60)	4871(7)	7318(6)	8344(3)	37(2)
C(61)	5277(6)	10175(5)	7959(3)	30(2)
C(62)	6006(7)	10372(7)	7690(3)	41(2)
C(63)	5728(8)	11068(7)	7499(4)	55(3)
C(64)	6843(8)	10507(8)	7885(3)	54(3)
C(65)	6117(8)	9731(8)	7416(3)	55(3)
C(66)	3293(7)	11676(6)	7694(3)	35(2)
C(67)	3730(8)	12249(6)	7498(3)	44(2)
C(68)	4280(8)	12679(7)	7694(3)	48(2)
C(69)	4386(8)	12562(6)	8077(3)	46(2)
C(70)	3937(7)	12012(5)	8249(3)	34(2)
C(23A)	3850(20)	13662(19)	8858(6)	55(4)
C(24A)	3842(19)	14144(15)	9533(7)	43(4)
C(25A)	2463(13)	13981(16)	9256(8)	45(3)
H(2)	5680	10291	9744	33
H(28)	2413	8004	8240	51
H(3B)	8544	9584	9469	59
H(3C)	7971	10278	9593	59
H(3A)	7825	9915	9193	59
H(4A)	6998	8855	10127	56
H(4C)	7449	9646	10157	56
H(4B)	8026	8941	10057	56
H(5B)	6949	8213	9534	68
H(5C)	7941	8386	9422	68
H(5A)	7159	8635	9155	68

H(8B)	3257	7395	9951	73
H(8C)	4147	7101	10132	73
H(8A)	4115	7307	9700	73
H(9C)	5412	7982	10252	71
H(9B)	5356	8787	10074	71
H(9A)	5416	8081	9810	71
H(10C)	3983	8962	10483	75
H(10B)	4044	8129	10622	75
H(10A)	3164	8424	10433	75
H(13B)	7665	11356	8998	53
H(13C)	8167	12127	9007	53
H(13A)	7352	12013	8734	53
H(14A)	7613	11511	9679	54
H(14B)	6994	12114	9867	54
H(14C)	7916	12352	9695	54
H(15B)	7332	13274	9250	69
H(15C)	6380	13168	9427	69
H(15A)	6518	13080	8989	69
H(18B)	3620	11233	11066	85
H(18C)	4302	10714	11277	85
H(18A)	3728	10393	10943	85
H(19A)	5635	11894	10695	71
H(19C)	5413	11709	11119	71
H(19B)	4720	12145	10870	71
H(20A)	5124	9990	10700	71
H(20C)	5723	10437	10986	71
H(20B)	5847	10551	10549	71
H(23A)	4406	13448	8847	84
H(23C)	4775	13747	9234	84
H(23B)	4336	14304	8945	84
H(24B)	3097	14680	9435	68
H(24C)	3747	14227	9697	68
H(24A)	2730	14021	9684	68
H(25C)	2829	14286	8798	77
H(25B)	2149	13732	8987	77
H(25A)	2870	13427	8704	77
H(28A)	117	9329	9736	80
H(28C)	54	10072	9972	80
H(28B)	-231	9307	10155	80
H(29A)	1056	8345	9911	90
H(29C)	977	8367	10354	90
H(29B)	1909	8482	10160	90
H(30A)	1871	9621	10580	100
H(30C)	854	9543	10677	100

H(30B)	1214	10281	10490	100
H(31)	1140	10832	8897	34
H(32)	-314	10911	9060	42
H(33)	-720	11460	9623	36
H(34)	367	11885	10013	39
H(35)	1811	11743	9857	35
H(38A)	984	12273	7601	97
H(38C)	648	12499	8006	97
H(38B)	1	12553	7658	97
H(39B)	-905	11788	8127	104
H(39C)	-55	11710	8383	104
H(39A)	-558	10991	8242	104
H(40B)	-65	11342	7280	118
H(40C)	-936	11323	7526	118
H(40A)	-297	10626	7518	118
H(43A)	-1049	7785	8874	82
H(43C)	-633	8469	9090	82
H(43B)	-19	7813	8949	82
H(44A)	-840	9453	8262	90
H(44C)	-795	9530	8704	90
H(44B)	-1572	9074	8515	90
H(45A)	-635	8319	7962	92
H(45C)	-1279	7867	8227	92
H(45B)	-288	7605	8175	92
H(48B)	1927	8980	6765	104
H(48C)	1298	8490	7020	104
H(48A)	1783	8129	6672	104
H(49B)	1868	7478	7367	117
H(49C)	2876	7461	7486	117
H(49A)	2587	7159	7087	117
H(50A)	3379	8398	6663	120
H(50B)	3736	7816	6959	120
H(50C)	3828	8678	7038	120
H(53B)	2516	5955	9142	139
H(53C)	3045	6711	9116	139
H(53A)	3329	6027	8865	139
H(54C)	2596	5586	8445	133
H(54B)	2825	6286	8194	133
H(54A)	1839	5994	8218	133
H(55A)	991	6699	8565	147
H(55C)	1259	6859	8986	147
H(55B)	1181	6031	8842	147
H(58A)	4634	7451	9049	69
H(58C)	5310	8086	9160	69

H(58B)	5664	7309	9017	69
H(59B)	6491	7853	8435	59
H(59C)	6284	8632	8621	59
H(59A)	5995	8474	8201	59
H(60A)	4789	7487	8088	55
H(60C)	4315	7131	8440	55
H(60B)	5309	6925	8348	55
H(63B)	6216	11261	7352	83
H(63C)	5555	11432	7685	83
H(63A)	5231	10965	7335	83
H(64B)	6961	10101	8056	82
H(64C)	6804	10968	8024	82
H(64A)	7318	10542	7703	82
H(65A)	5599	9699	7256	83
H(65C)	6184	9271	7555	83
H(65B)	6637	9814	7263	83
H(66)	2922	11354	7559	42
H(67)	3638	12324	7240	53
H(68)	4596	13060	7574	57
H(69)	4771	12865	8216	56
H(70)	4011	11933	8507	41
H(23E)	4275	13260	8851	82
H(23F)	4153	14131	8820	82
H(23D)	3414	13592	8662	82
H(24D)	4478	14092	9515	64
H(24F)	3645	13980	9778	64
H(24E)	3681	14660	9497	64
H(25E)	2475	14512	9212	68
H(25F)	2225	13884	9504	68
H(25D)	2093	13743	9069	68

Table S3. Selected bond lengths (Å) for complex **1**

Sr(1)-O(21)	2.524(7)
Sr(1)-O(15)	2.529(6)
Sr(1)-O(11)	2.576(7)
Sr(1)-O(8)	2.580(7)
Sr(1)-O(24)	2.609(6)
Sr(1)-O(29)	2.625(7)
Sr(1)-O(32)	2.673(6)
Sr(1)-O(22)	2.680(6)
Sr(1)-O(25)	2.997(6)

Sr(2)-O(31)	2.474(6)
Sr(2)-O(9)	2.563(6)
Sr(2)-O(1)	2.564(6)
Sr(2)-O(25)	2.565(6)
Sr(2)-O(3)	2.567(6)
Sr(2)-O(13)	2.584(6)
Sr(2)-O(32)	2.593(6)
Sr(2)-O(11)	2.708(6)

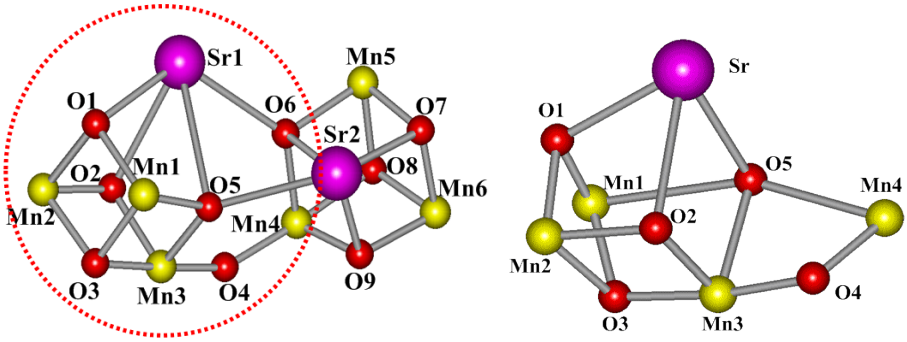

Fig. S3. Core of complex **1** (left) and OEC in Sr^{2+} -containing PSII (right). Mn, Sr and O are shown in yellow, violet and red, respectively.

Table S4. The calculated bond valence sum (BVS) for the core of complex **1** in **Fig.3** (left)*

Atom	BVS	Assignment
Mn1	4.011	Mn^{IV}
Mn2	4.023	Mn^{IV}
Mn3	4.290	Mn^{IV}
Mn4	4.164	Mn^{IV}
Mn5	4.075	Mn^{IV}
Mn6	4.298	Mn^{IV}
O1	1.752	O^{2-}
O2	1.939	O^{2-}
O3	2.065	O^{2-}
O4	1.904	O^{2-}
O5	1.915	O^{2-}
O6	1.992	O^{2-}
O7	1.874	O^{2-}
O8	2.022	O^{2-}
O9	1.840	O^{2-}

*: **Note:** Bond valence sum calculations are based on the Subroutine **Calc_BVS** of the program **Bond_Str**, J.Rodríguez-Carvajal-LLB, France, Version: March 2005.

Table S5. Selected bond lengths (Å) in the core of complex **1** and the OEC in Sr^{2+}-containing PS II as shown in **Fig. S3**.

	Complex **1**	OEC
Sr1-Mn1	3.505	3.557
Sr1-Mn2	3.501	3.452
Sr1-Mn3	3.548	3.646
Sr1-Mn4	4.058	3.993
Mn1-Mn2	2.743	2.747
Mn1-Mn3	2.846	3.335
Mn2-Mn3	2.738	2.909
Mn3-Mn4	3.375	2.896
O4-Mn3	1.772	1.858
O4-Mn4	1.742	1.917
O1-Mn1	1.875	1.896
O1-Mn2	1.830	1.900
O2-Mn2	1.822	1.830
O2-Mn3	1.845	1.713
O3-Mn1	1.874	2.022
O3-Mn2	1.891	1.954
O3-Mn3	1.901	1.877
O5-Mn1	1.866	2.680
O5-Mn3	1.871	2.358

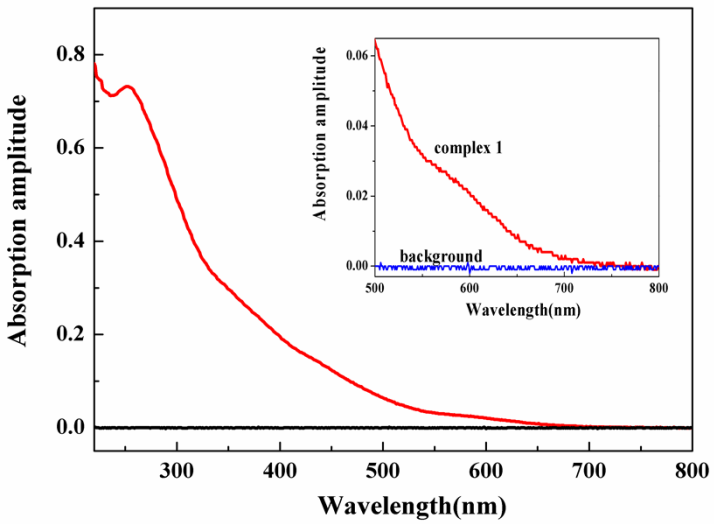

Fig. S4. UV-vis absorption spectrum of 20 μM complex **1** in CH_3CN. (Inset is the enlarged spectrum of complex **1** in the visible region.).

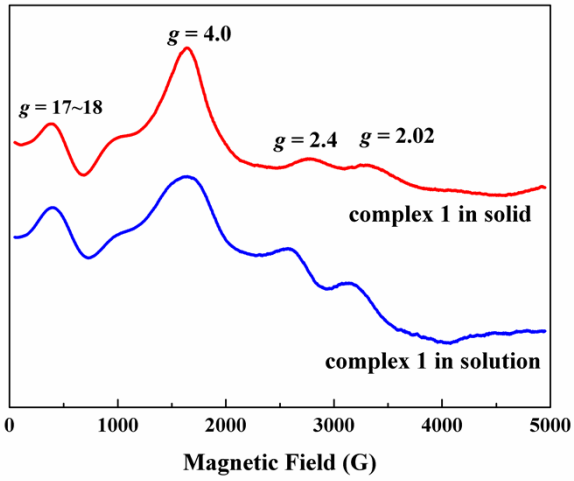

Fig. S5. EPR spectra of complex **1** in solid (red spectrum) and 5mM in ethyl acetate solution (blue spectrum). EPR conditions: Microwave frequency, 9.338 GHz; Microwave power, 10 mW; Modulation amplitude, 10 G; Modulation frequency, 100 kHz; Temperature, 77 K.

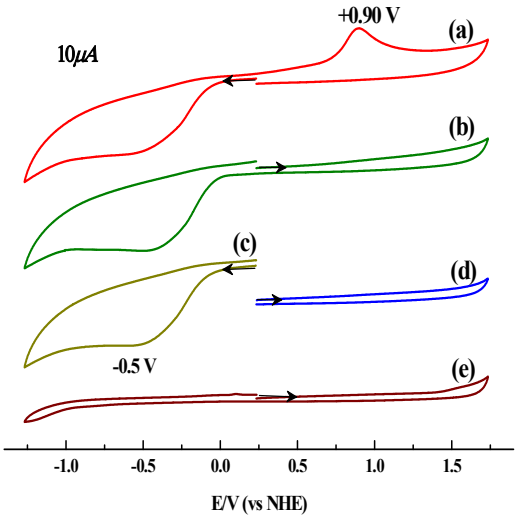

Fig. S6. Cyclic voltammogram (CV) measurements. The arrows indicate the scan direction. (a), (b), (c) and (d) are the CV of complex **1**. (e) is the CV of background without addition of complex **1**. Potentials are referenced to NHE. Scan rate: 100mV/s.

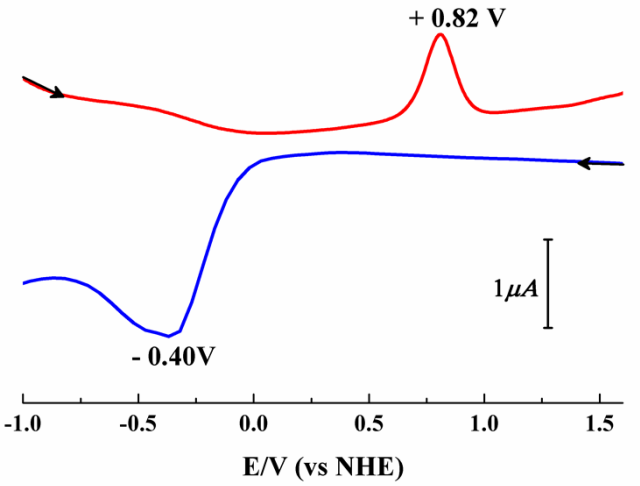

Fig. S7. Differential pulse voltammogram (DPV) of complex **1**. The arrows show the scan direction. Potentials are referenced to NHE. Scan rate: 10mV/s.