Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Redox reactions of pyrazine bridged Ru^{III}(edta) binuclear complex: spectral, electrochemical and spectro-electrochemical studies

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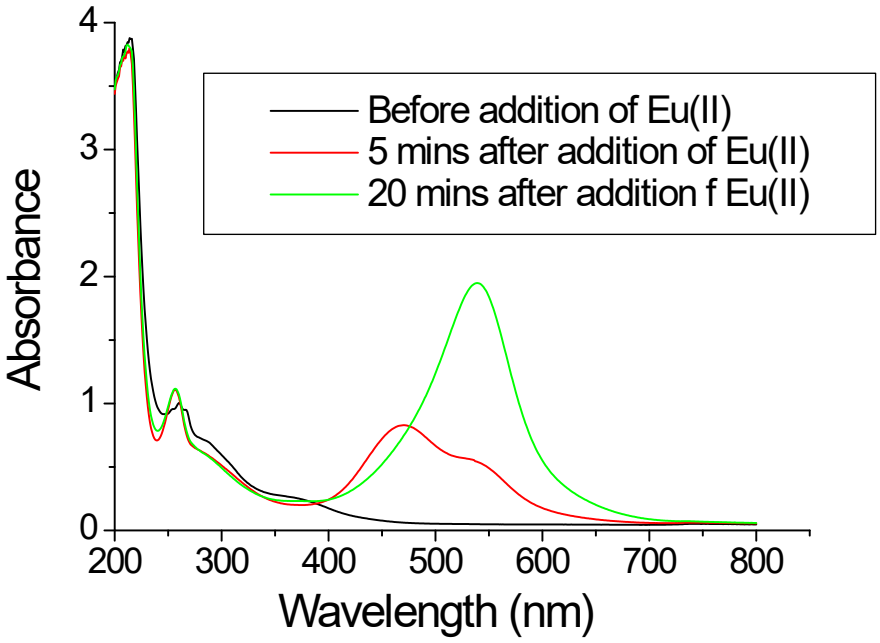


Fig. S1 Spectral changes that occurred during the reduction of $[(edta)Ru^{III}pzRu^{III}(edta)]^{2-}$ (0.1 mM) with Eu^{II} (0.4 mM) at room temperature. pH = 6.0 (acetate buffer)

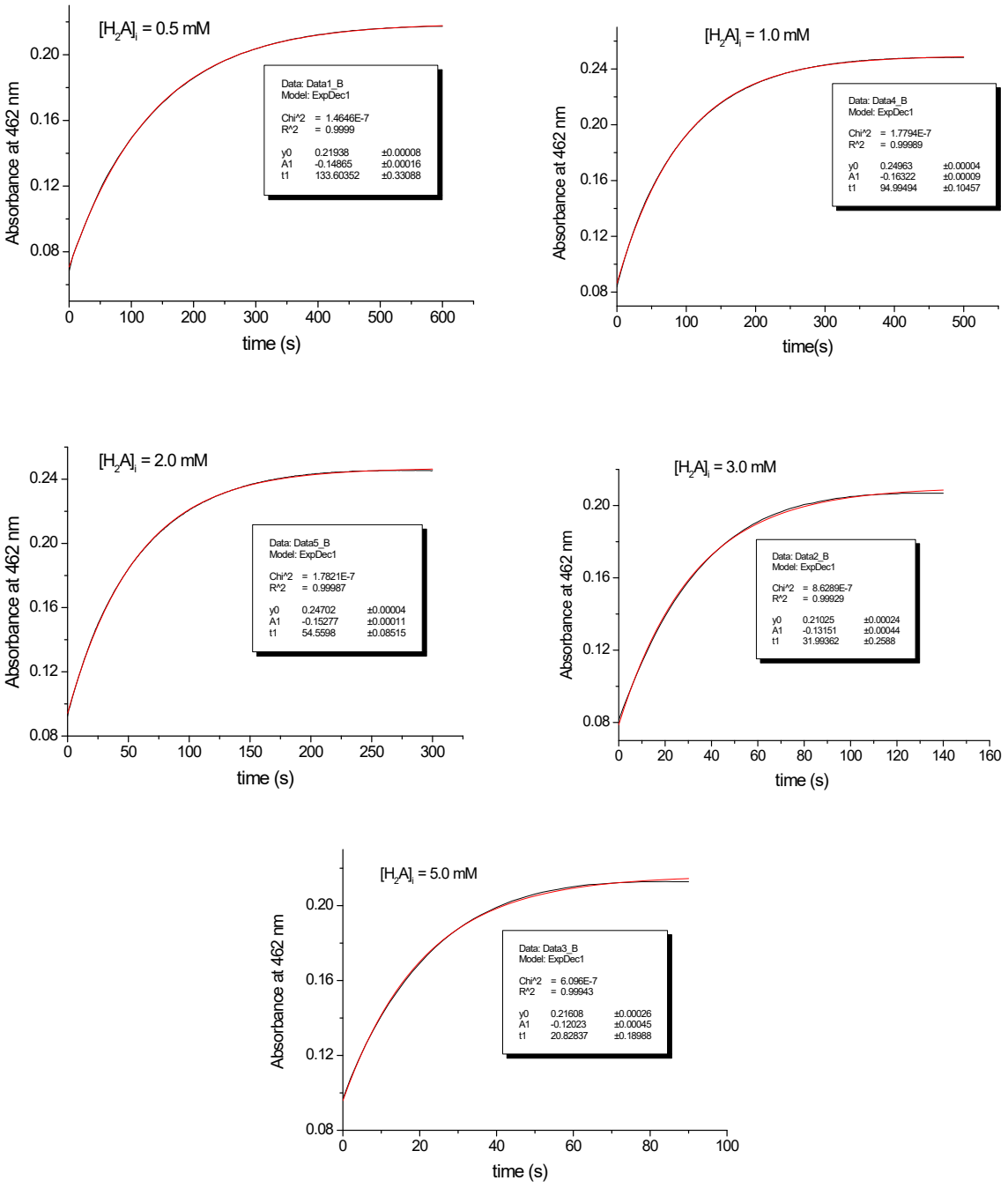


Fig. S2 Time versus absorbance plot (growth recorded at 462 nm) pertaining to the reduction of Ru^{III}-Ru^{III} to Ru^{II}-Ru^{III} as a function of ascorbic acid concentration at 25 °C and pH 6.0. [Ru^{III}-Ru^{III}] = 0.05mM

S1 Magnetic moment measurements studies

Magnetic moment measurements studies were performed using the SQUID magnetometer (MPMS, Quantum Design). The solution of Ru^{III}-Ru^{III} was electrolyzed in a quartz tube under argon. After electrolysis the tube containing the electrolyzed solution tightly under argon was transferred to the pre-calibrated (with the empty tube and with the solvent) magnetometer for measurements. The susceptibility data were acquired at room temperature, corrected to the background signals and underlying diamagnetism[1], and transformed to the effective magnetic moment. The value of magnetic moment at room temperature for Ru(III) -Ru(III) units is 2.59 μB confirm the presence of two non-pair electron in such system. After the one electron reduction process the observed value of magnetic moment is 1.69 μB correspond to one non-pair electron in Ru(II) -Ru(III) species and finally the measurement procedure shown negative value of magnetization adequate to diamagnetic configuration of Ru(II) – Ru(II) unit.

Reference 1 G. A. Bain and J. F. Berry, *J. Chem. Educ*., 2008, **85**, 532–536

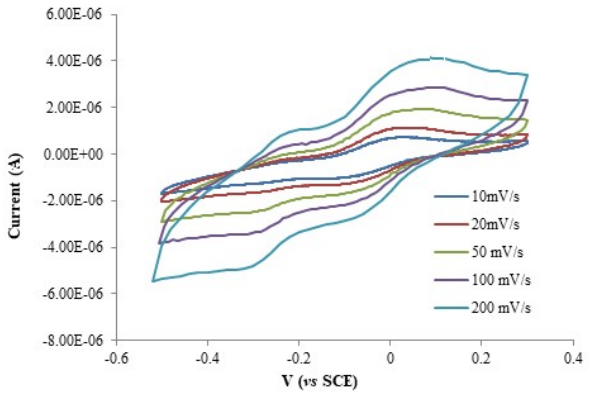


***Fig. S3** Cyclic voltammograms of $[(edta)Ru^{III}pzRu^{III}(edta)]^{2-}$ (Ru^{III}-Ru^{III}) at different scan rate. [Ru^{III}-Ru^{III}] = 0.1mM, pH 6.0 (acetate buffer), $[_{NaClO4}]$ = 0.1M.

*Electrochemical analysis was performed with an Autolab PGSTAT302N potentiostat-galvanostat**,** a single compartment gastight electrochemical cell was equipped with a glassy carbon working electrode, a platinum wire as counter and a SCE reference electrode. Electrochemical measurements were performed strictly under argon atmosphere. All the solutions were prepared using high purity demineralised Milli-Q water.

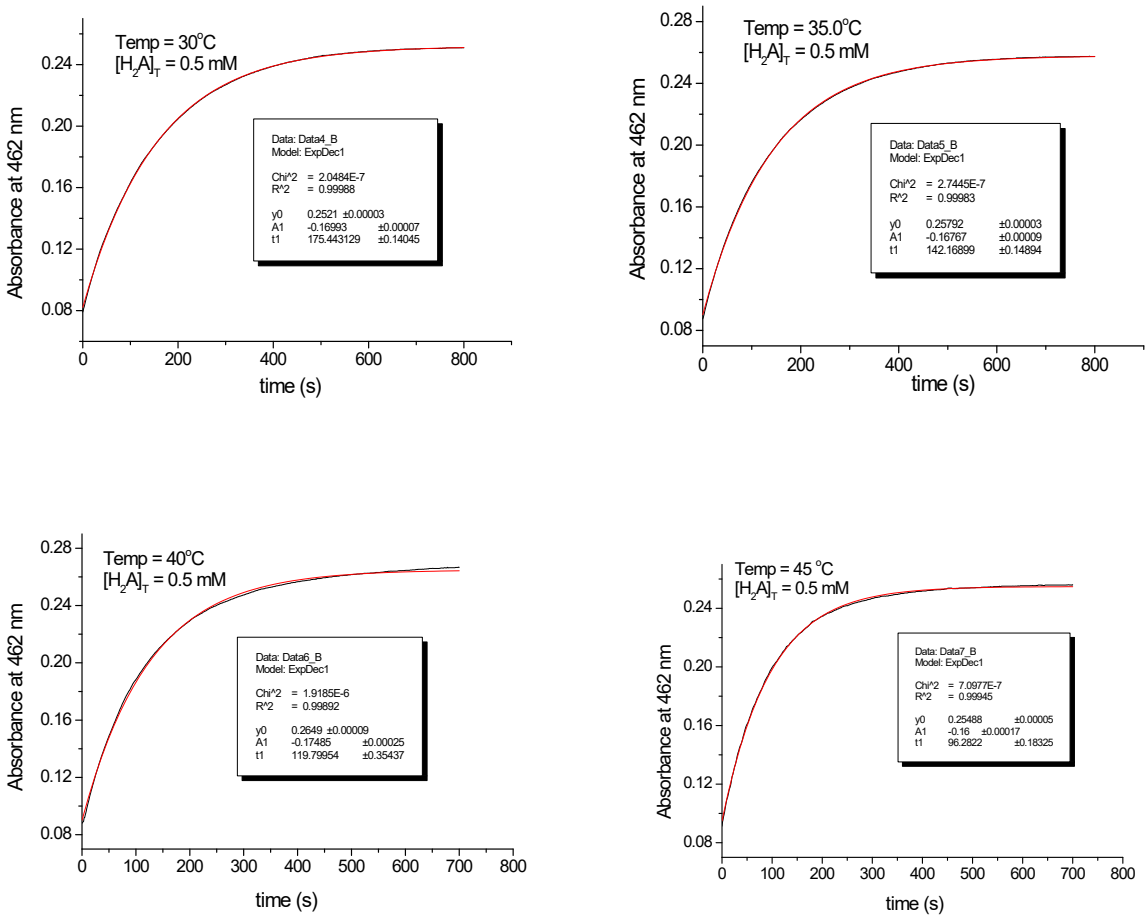


Fig. S4 Time versus absorbance plots (growth recorded at 462 nm) pertaining to the reduction of Ru^{III}-Ru^{III} to Ru^{II}-Ru^{III} by ascorbic acid at a different temperature pH 6.0. $[H_2A]_i$ = 0.5 mM [Ru^{III}-Ru^{III}] = 0.05mM.

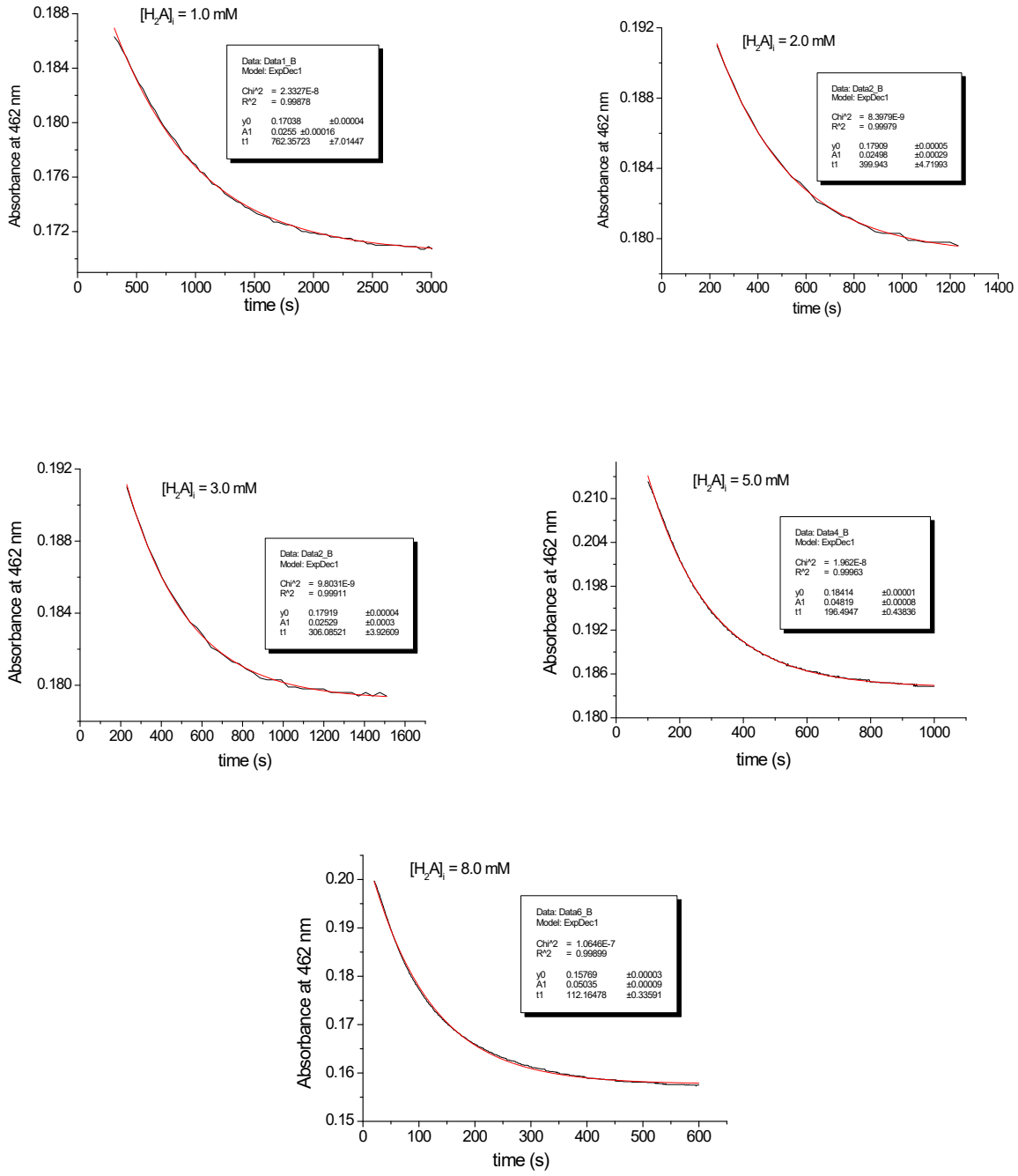


Fig. S5 Time versus absorbance plots (decay recorded at 462 nm) pertinent to the reduction Ru^{II}-Ru^{III} to Ru^{II}-Ru^{II} as a function of ascorbic acid concentration at 25 °C and pH 6.0. [Ru^{III}-Ru^{III}] = 0.05 mM

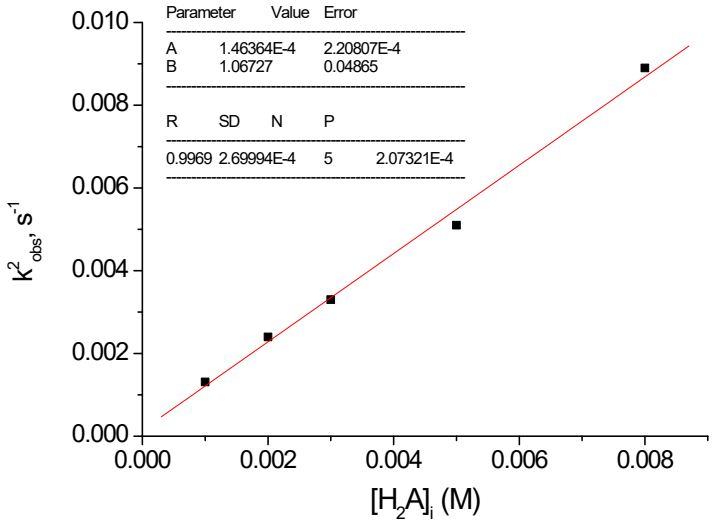


Fig. 6 Plot of k^2_{obs} (estimated from the traces shown in Fig. S6) versus $[H_2A]_i$ for the reduction of Ru^{II}-Ru^{III} by H_2A at 25 °C and pH 6.0. [Ru^{III}-Ru^{III}] = 0.05mM

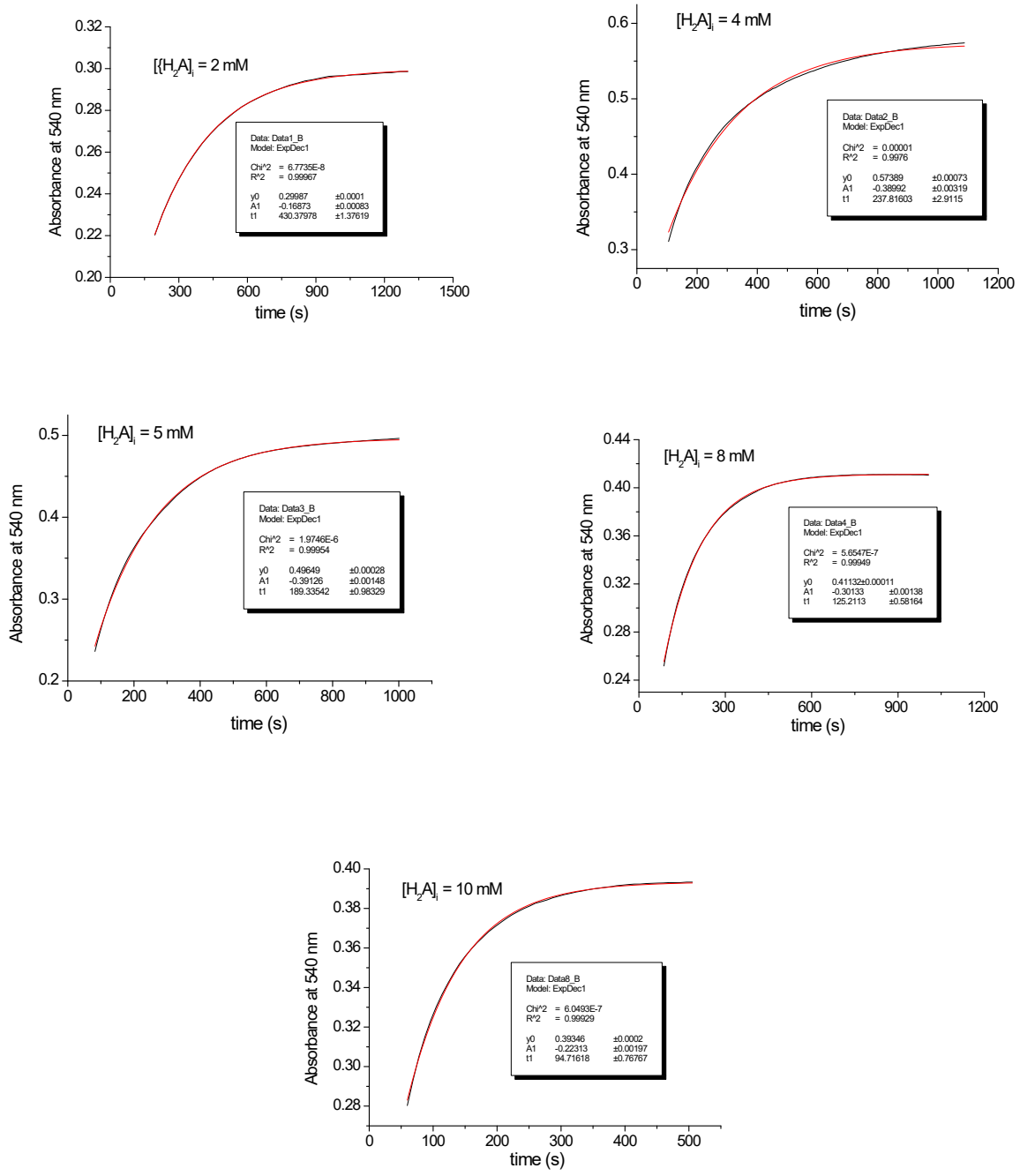


Fig. S7 Time versus absorbance traces (growth recorded at 540 nm) pertinent to the reduction of Ru^{II}-Ru^{III} to Ru^{II}-Ru^{II} as a function of ascorbic acid concentration at 25 °C and pH 6.0. [Ru^{III}-Ru^{III}] = 0.05 mM

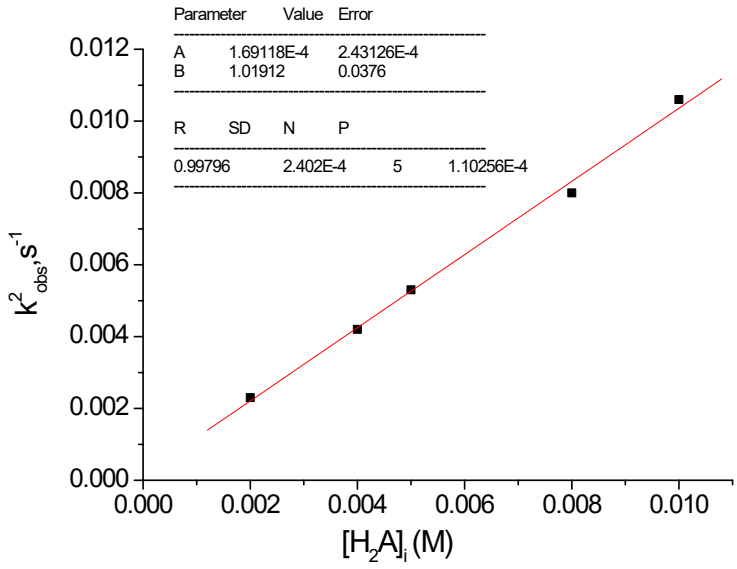
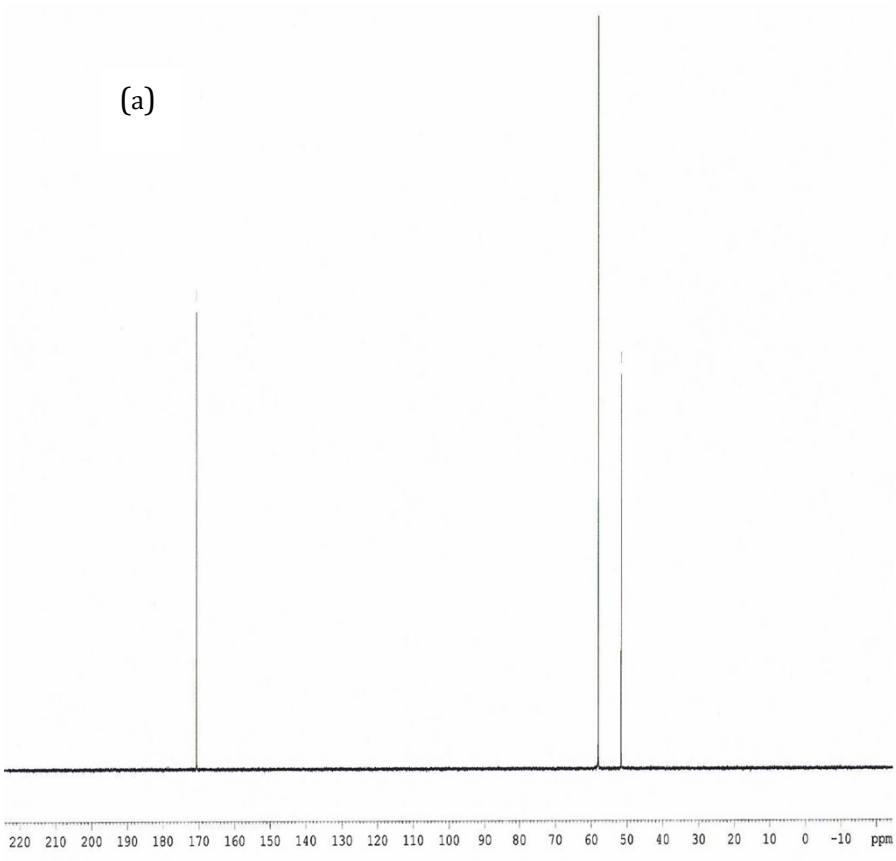
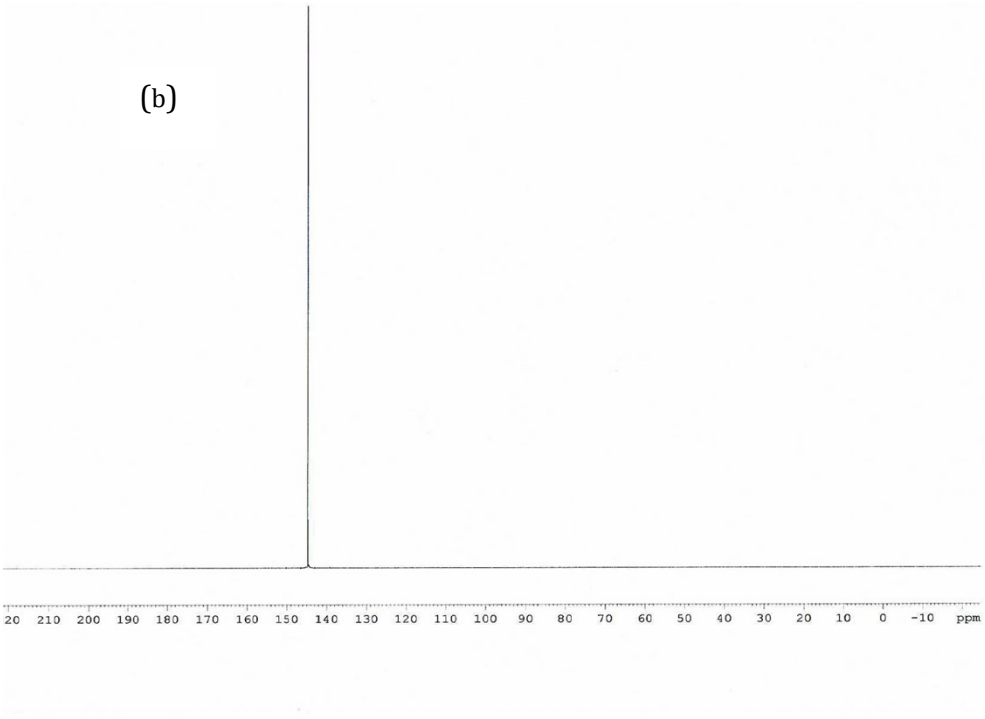


Fig. S8 Plot of k^2_{obs} (estimated from the traces shown in Fig. S8) versus $[H_2A]_i$ for the reduction of Ru^{II}-Ru^{III} by H_2A at 25 °C and pH 6.0. [Ru^{III}-Ru^{III}] = 0.05mM

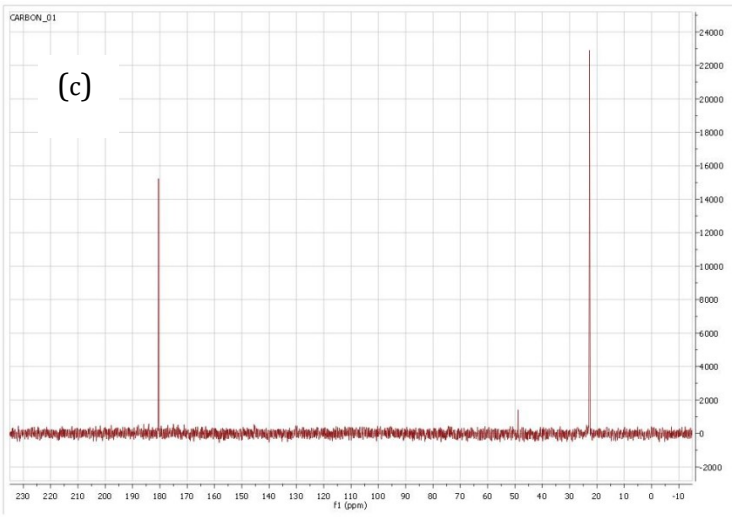
(a)


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

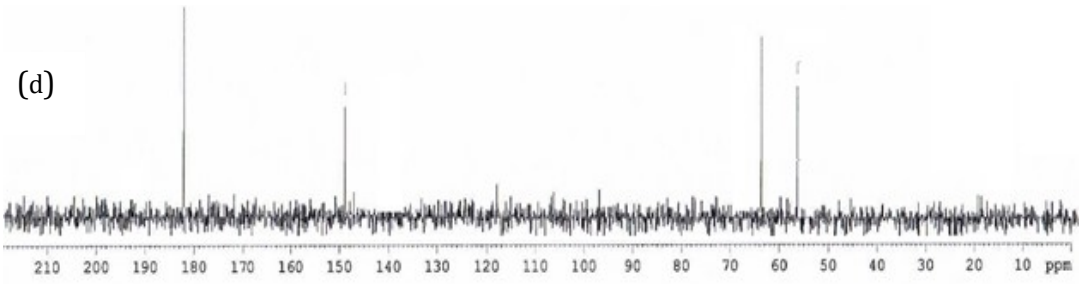
(b)


20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

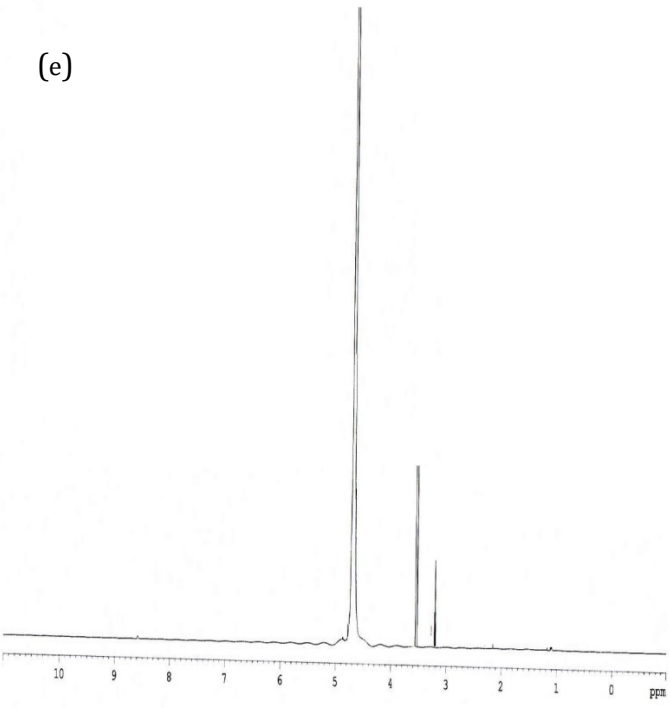
(c)


CARBON_01
f1 (ppm)

(d)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

(e)


10 9 8 7 6 5 4 3 2 1 0 ppm

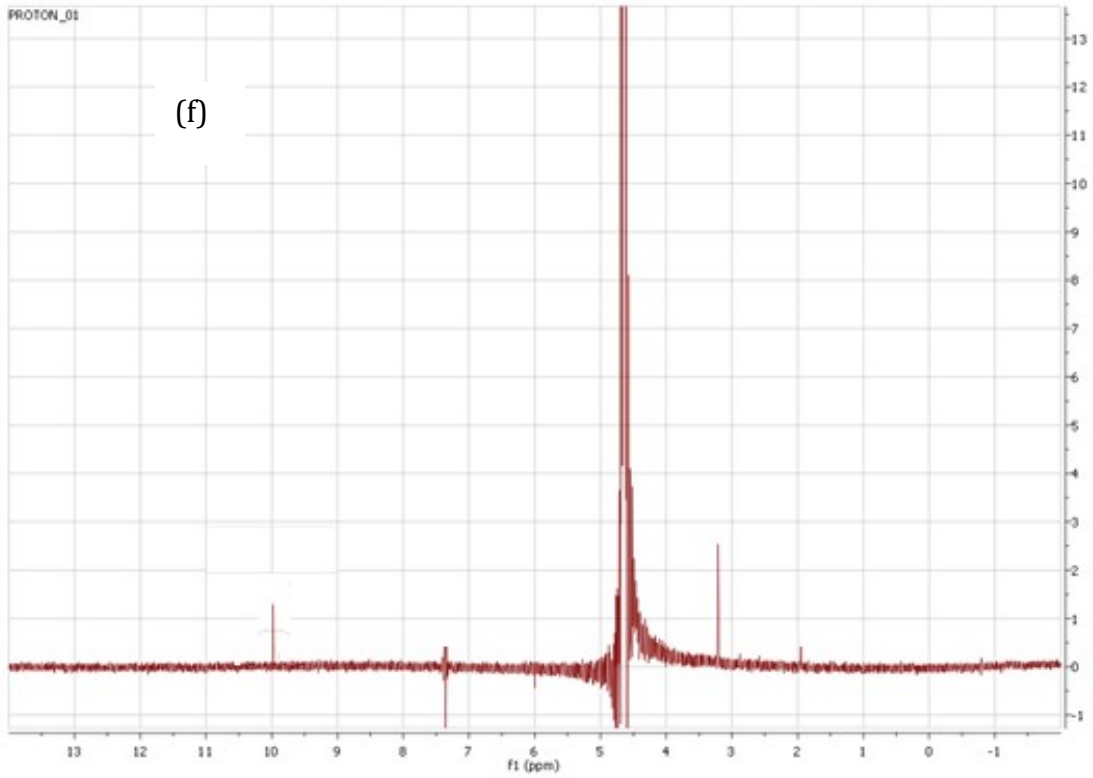


Fig. S9 (a) ^{13}C NMR spectra of Na_4edta, (b) ^{13}C NMR spectra of pyrazine, (c) ^{13}C NMR spectrun of the Ru^{II}-Ru^{II} dimer complex electrochemically generated by reducing the deoxygenated solution of Ru^{III}-Ru^{III} (0.5 mM) at -0.4V (vs SCE), (d) ^{13}C NMR spectrun of the Ru^{II}-Ru^{II} dimer complex generated by reducing the deoxygenated solution of Ru^{III}-Ru^{III} (2.0 mM) by Eu(II), (e) ^{1}H NMR spectra of the Na_4edta and (f) ^{1}H NMR spectra of the solution of the Ru^{II}-Ru^{II} dimer complex. NMR spetra were recorded on 600 MHz Bruker Avance II spectrometer using D_2O, and TMS as standard.

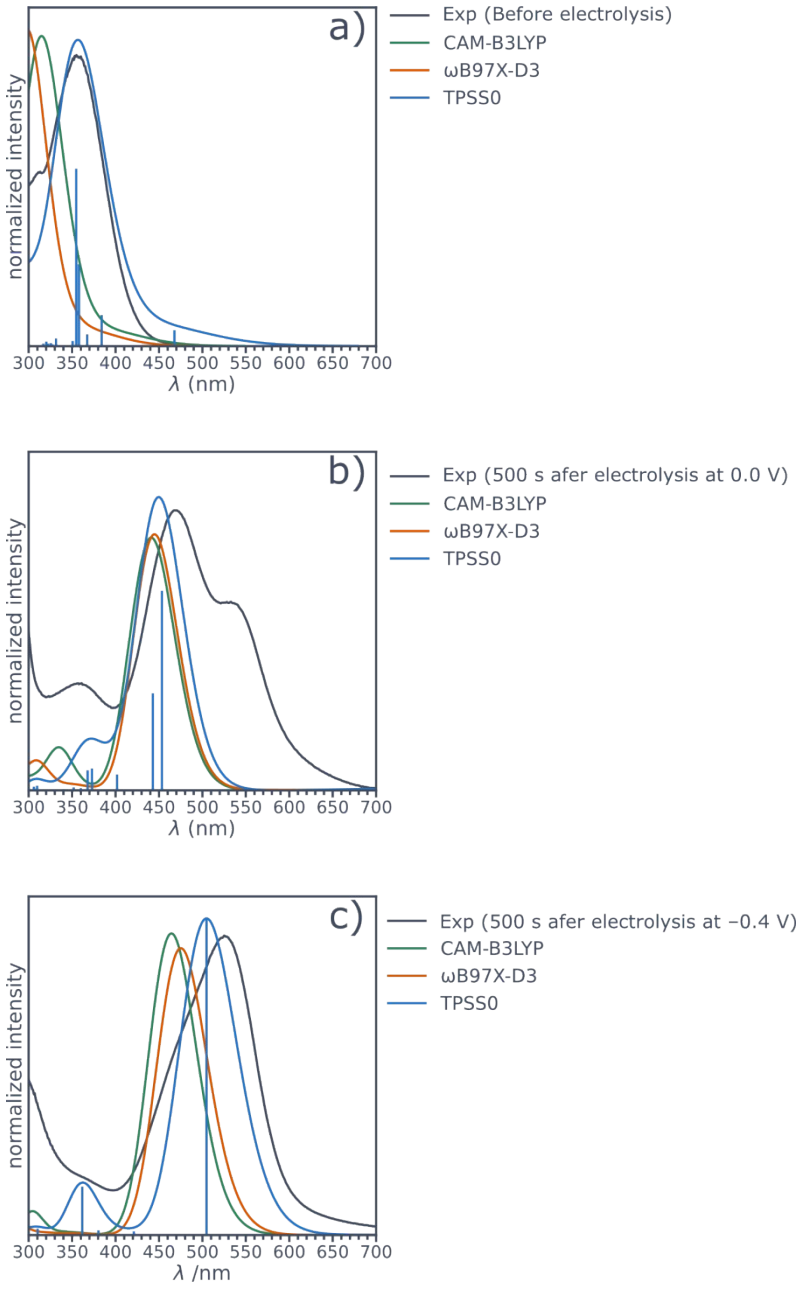


Fig. S10 Experimental and theoretically computed UV-vis absorption spectra: Ru^{III}-Ru^{III} (a), Ru^{II}-Ru^{III} (b) and Ru^{II}-Ru^{II} (c). The theoretically predicted spectra were simulated by associating a single Gaussian to each computed transition. The transitions computed at the TPSS0 theory level are shown.

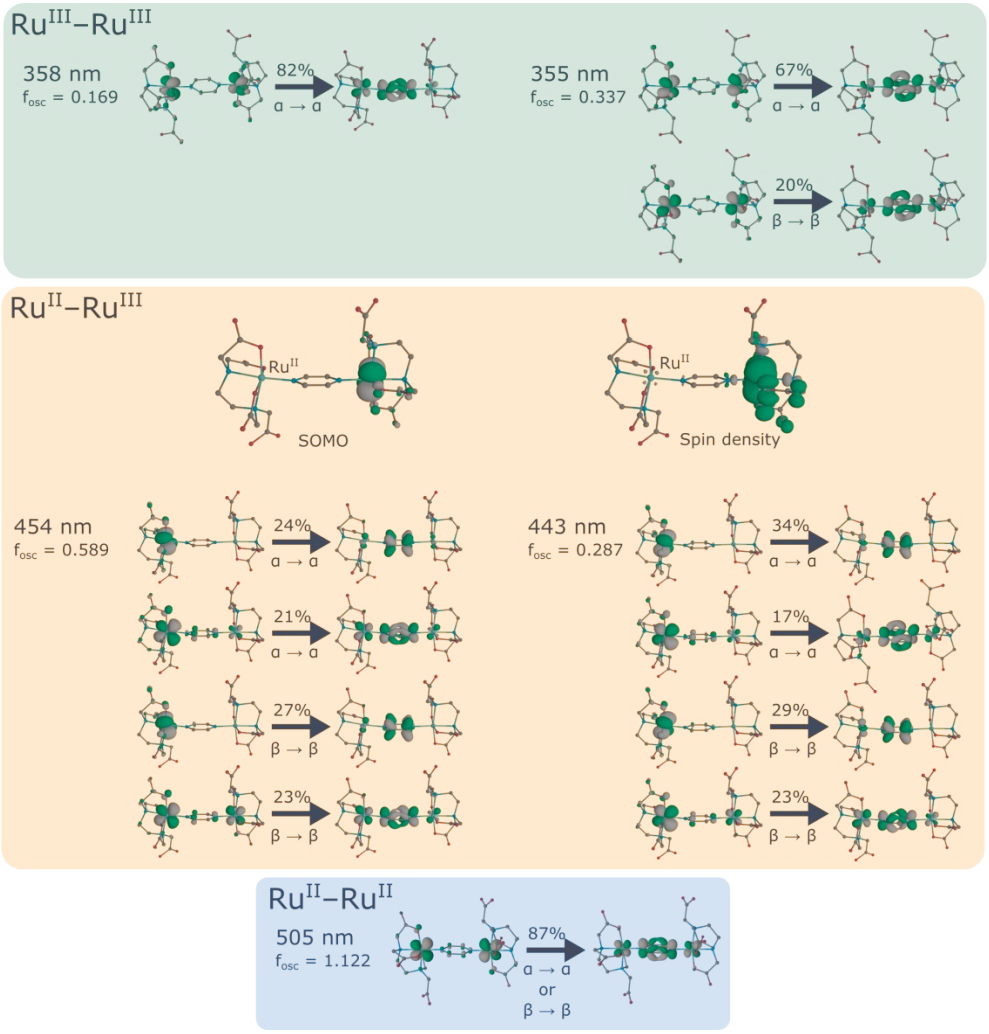


Fig. S11 Natural transition orbitals (NTOs) from the time-dependent TPSS0 calculations picturing the electronic excited states for Ru^{III}-Ru^{III}, Ru^{II}-Ru^{III} and Ru^{II}-Ru^{II}. For Ru^{II}-Ru^{III} singly occupied molecular orbital (SOMO) and spin density are shown to distinguish between the Ru^{II} and Ru^{III} center. All hydrogen atoms were omitted for clarity.

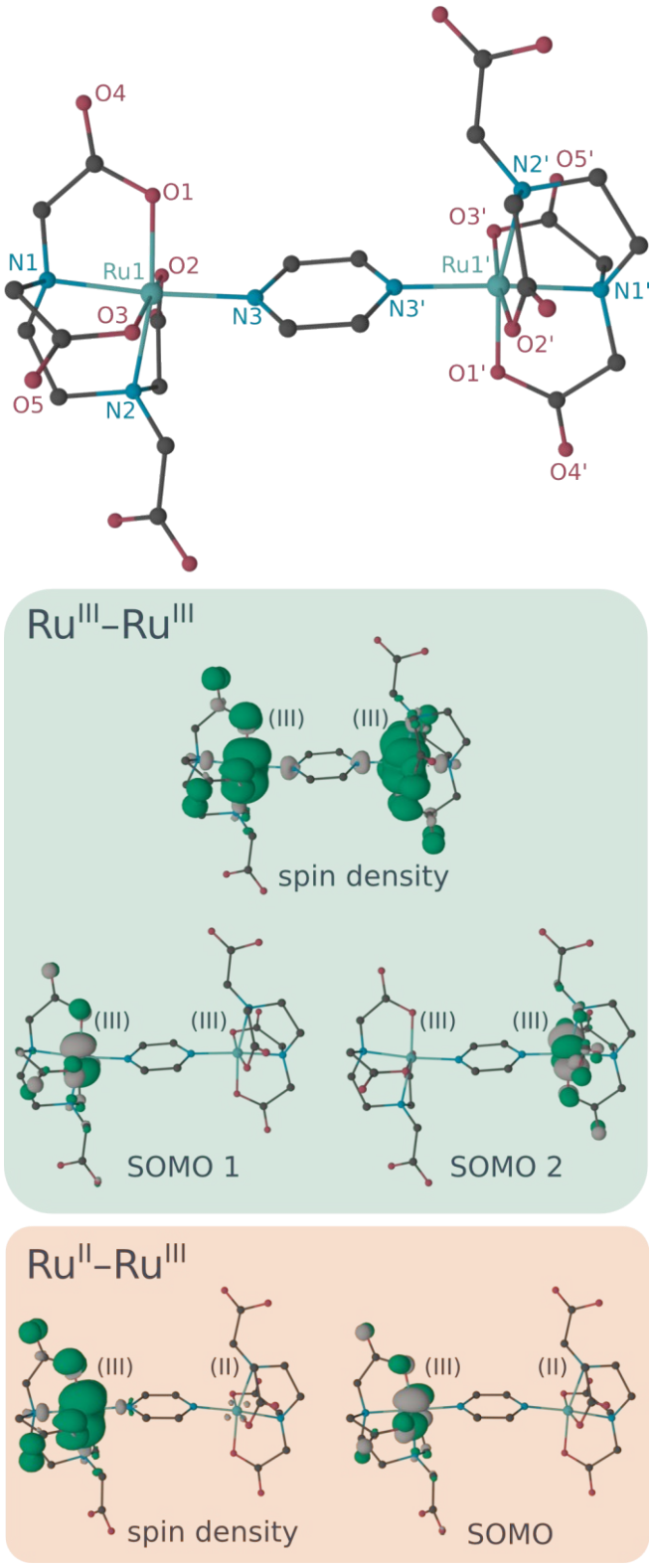


Fig. S12 Results of the DFT calculations with the hybrid functional TPSS0: molecular model with atom label, the singly occupied molecular orbital (SOMO) isosurfaces contoured at 0.05 a.u. and spin densities isosurfaces contoured at 0.001 a.u.; green for positive and gray for negative. All hydrogen atoms were omitted for clarity.

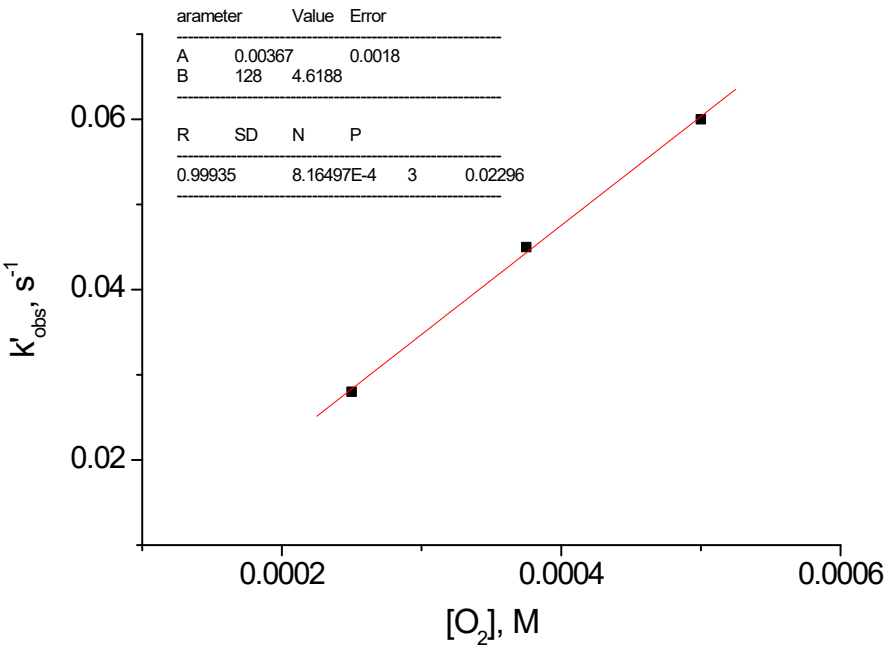


Fig. S13 Plot of k'_{obs} versus $[O_2]$ for the reaction of Ru^{II}-Ru^{II} with O_2 at 25 °C and pH 6.0. [Ru^{III}-Ru^{III}] = 0.025mM

Table S1. Selected bond lengths and the Löwdin spin populations for selected atoms. All calculated at the TPSS0 theory level.

		Ru^{III}–Ru^{III}	Ru^{II}–Ru^{III}	Ru^{II}–Ru^{II}
Bond length	Ru–N1	2.060	2.072	2.087
	Ru'–N1'	2.060	2.087	2.087
	Ru–N2	2.170	2.171	2.140
	Ru'–N2'	2.169	2.137	2.140
	Ru–N3	2.047	2.067	2.016
	Ru–N3'	2.053	1.965	2.016
	Ru–O1	1.960	1.977	2.077
	Ru'–O1'	1.963	2.049	2.077
	Ru–O2	2.017	2.020	2.094
	Ru'–O2'	2.018	2.083	2.094
	Ru–O3	1.983	1.996	2.093
	Ru–O3'	1.983	2.077	2.093
Spin population	Ru	0.834	0.845	–
	Ru'	0.834	-0.006	–
	N1	-0.009	-0.008	–
	N1'	-0.009	0.000	–
	N2	-0.003	-0.003	–
	N2'	-0.003	0.000	–
	N3	-0.009	-0.002	–
	N3'	-0.009	-0.001	–
	O1	0.061	0.048	–
	O1'	0.060	0.000	–
	O2	0.036	0.034	–
	O2'	-0.002	0.000	–
	O3	0.050	0.044	–
	O3'	0.050	0.000	–
	O4	0.026	0.023	–
	O4'	0.026	0.000	–
	O5	0.024	0.024	–
	O5'	0.024	0.000	–

S2 Detection of H_2O_2

Detection of H_2O_2 in the reaction of Ru^{II}-Ru^{II} with dissolved oxygen was achieved by using Quantofix® peroxides test sticks (Marks) ranging. A solution of Ru^{III}-Ru^{III} (5 mL; 2.5 mM) was pre-reduced with stoichiometric amount of Eu(II) under argon. Upon completion of the reduction (aliquot of the reacting solution was diluted and checked spectrophotometrically), the resultant solution of Ru^{II}-Ru^{II} complex was bubbled with O_2 for 15 mins. Then the solution was kept in equilibration for another 15 mins. Evidence of H_2O_2 formation was obtained by immersing the sick in to the resultant solution by noting the color change in the stick. A blank experiment was performed without purging O_2, but with argon.

S3 XYZ coordinates of the optimized structures of the Ru^{II}-Ru^{II}, Ru^{II}-Ru^{III} and Ru^{III}-Ru^{III} compexes

Ru^{II}–Ru^{II}

Ru	6.16422878145120	8.72901521093971	4.96947546624866
N	7.47457409655345	7.08180788809815	5.35600305343233
C	8.71393927465817	7.40812640254069	4.61866316285153
C	8.47845150466740	8.23361432134151	3.33741596822492
O	9.23654410228699	8.05850982951111	2.39494122586825
O	7.51025435772426	9.06932373846292	3.40162522569731
C	7.66359767276957	6.91625195560957	6.79672096495895
C	8.41894165268971	5.70607413671563	7.29971878521496
O	8.41843818860387	5.34563085512419	8.44509355444757
O	9.12790666981354	5.05505711210875	6.35828453206693
C	6.74462045213496	5.92938927271976	4.77161439581218
C	6.01390763794301	6.31315333969197	3.49281018653002
C	3.89190071668668	7.00324949596352	4.52211157617407
N	5.08600238865450	7.41610460854131	3.75797347059301
C	4.03805424893426	7.11949120790169	6.05047370378022
O	3.35412042996549	6.39017540526374	6.75290952691165
O	4.86113982053408	8.01847388269529	6.44477685522883
C	4.73489645800072	8.24581864264294	2.59380294793520
C	4.24644290456682	9.63698647355640	3.06793614293523
O	3.45062859815270	10.23839662658141	2.36362043014759
O	4.75798264000696	10.03471563286505	4.17400500406614
N	7.09113771729232	10.04560519937713	6.18315484725532
C	8.06496356039428	10.88061829855869	5.75540759883010
C	6.74853067716751	10.16017377565885	7.48631976923076
N	8.33319605366767	11.90223991581262	7.90053193804275
C	7.36180656751481	11.06480885989020	8.32907855457614
C	8.67855546903141	11.78498475968829	6.59829227465293
Ru	9.23848550012927	13.23905535012153	9.10839587161523
N	7.91677242190044	14.86886592117111	8.68786453170567
C	6.67204473357540	14.53823928485070	9.41420769525427
C	6.90058873586223	13.73043647682046	10.70784848928258
O	6.12896623515897	13.90795651373161	11.63879165772570
O	7.87860568777179	12.90477578379885	10.66542655658308
C	7.74316685790656	15.01693564921893	7.24323933693853
C	6.98423033097146	16.21534121032465	6.71811863730529
O	6.99699902595477	16.56451709002721	5.56934689338982
O	6.25660620154943	16.86884707661426	7.64342533853246
C	8.62823627572181	16.03505903718044	9.26764364513598
C	9.34842449862223	15.67286631615898	10.55852592003533
C	11.48809241126254	14.99393500151506	9.55844322112858
N	10.29068163649781	14.57712506013787	10.31533998978649
C	11.36005676040952	14.85637879950390	8.03020191735513
O	12.04457387062788	15.58344477165680	7.32599761523964
O	10.55056981873165	13.94401106185764	7.63848740641538
C	10.63906166364232	13.76492161418470	11.49261831125810
C	11.14613852496365	12.37335049990654	11.03995683372788
O	11.94229235886914	11.78924068307656	11.75838508565291
O	10.64813408778907	11.95647635320625	9.93478469872404
H	9.32537743649601	8.03211943330329	5.27681537181830
H	9.28469775112169	6.51020130126861	4.37305489520665
H	6.67763399908259	6.91877309559144	7.27060484046797
H	8.18528703165380	7.79781755951324	7.17920744266472
H	9.57537293355746	4.33281685001377	6.81599037191451
H	7.43417711386673	5.10036308951840	4.57723519543189
H	6.01906325626634	5.59585746913493	5.51894402465642
H	6.72491638117629	6.64388467108252	2.73357891851901
H	5.48851415089713	5.42964644622511	3.09970941971563
H	3.58775467294074	5.98357067107264	4.26116153484310
H	3.07496888276010	7.67476400288572	4.24712766620033
H	5.64742223282526	8.40520701376785	2.01485658817005
H	3.96854183170623	7.77698649113786	1.96536580712873
H	8.32944787683481	10.79904061045510	4.70785913224578
H	5.95513768536867	9.50258528341833	7.82427083560073
H	7.09537933426895	11.14836337739871	9.37596993722894
H	9.47075788876329	12.44380575974795	6.25994311592417
H	6.07523584583799	13.90006277586799	8.75623551244367
H	6.08893551041313	15.43288033366281	9.64213734967469
H	8.73453080231344	15.01723486675090	6.78077517365362

H	7.23280439331561	14.12719407960356	6.86443594737563
H	5.80848166360320	17.58217156193822	7.17257715480234
H	7.92814124400838	16.85901588472490	9.44511030343269
H	9.35883767273817	16.36786830520532	8.52488571868714
H	8.63258974128886	15.34254357057486	11.31335391965129
H	9.86009157047485	16.56606885139530	10.94784314295847
H	11.77784888588551	16.02029859965938	9.80933269614561
H	12.30967844678146	14.33555755641599	9.85085139808372
H	9.72280909479700	13.60301557205604	12.06498310991241
H	11.39462438917019	14.24902851368160	12.12255266093454

Ru^{II}–Ru^{III}

Ru	6.04059251594548	8.70821131281894	4.85366619396804
N	7.46687289572645	7.20629660770129	5.50393104108252
C	8.76150320437091	7.58235702454834	4.88550710081517
C	8.58563524452037	8.30510590706391	3.55064534154476
O	9.44709765722278	8.24249748841599	2.70467576546294
O	7.47841802362724	8.97495342218053	3.46023181103827
C	7.54088096695198	7.12283934025817	6.97103105352089
C	8.33664450452214	5.99093332649571	7.58652372457622
O	8.23435238019401	5.67481322798249	8.73607385119653
O	9.18804918639002	5.38779200489869	6.74037977192245
C	6.89476455706107	5.95675650152123	4.92524514484582
C	6.24727535373671	6.18763330030075	3.56631312974848
C	3.98938616010477	6.76563743662290	4.37498298313311
N	5.20585721492322	7.22590782730580	3.67020495646183
C	4.03350365940172	7.01154863378451	5.88625474048793
O	3.38564805192333	6.32326955967121	6.63602438600465
O	4.78895969868458	8.01642005319861	6.24617474725760
C	4.88112492653348	7.93405331728980	2.41724497261550
C	4.32518739767234	9.33410512445127	2.74118821858848
O	3.53869157488847	9.86195995484625	1.99560623346636
O	4.81043106181091	9.87131719943334	3.83298673671656
N	6.82342526270319	10.19073265001002	6.06237402398309
C	7.73718488823305	11.06958972390538	5.60378446357207
C	6.49667227547008	10.28611656006914	7.36680068089402
N	8.04756837835443	12.06162330260637	7.75703351017005
C	7.09975278705923	11.19680219741095	8.20585399734195
C	8.34025502818194	11.98973601309047	6.43061389955335
Ru	9.08331704796846	13.22597778208518	8.95386483323377
N	7.92460476518450	15.01431648624301	8.79826474519833
C	6.70758570519537	14.74488318009081	9.59565881294830
C	6.92193412018043	13.76477424098742	10.76712448539981
O	6.20785128636700	13.88073622016776	11.74627032205973
O	7.82167320909170	12.86764810596139	10.57188197801125
C	7.64194627531386	15.30043672718110	7.39125914304415
C	6.84853747577302	16.53862993888757	7.03351155311862
O	6.50973980576581	16.79660947764261	5.91195426893888
O	6.54913896788027	17.33592625568457	8.07190882037185
C	8.79685081031231	16.05069288007670	9.41319885887576
C	9.57239431904532	15.49346376290239	10.59629803324596
C	11.53242885787601	14.70741092664541	9.33682060990878
N	10.36671614898449	14.33551632290364	10.16893802724034
C	11.25014469604433	14.72813312824534	7.82522550480521
O	11.91260348626143	15.46136955646654	7.11398476274920
O	10.32742307608326	13.91793434112459	7.44090978725231
C	10.73269985022136	13.39037136725832	11.23877285280562
C	11.04027095672814	12.00830236189531	10.62067403563392
O	11.81612295945910	11.26464858639053	11.18821614379405
O	10.40284464372652	11.76620587917768	9.52648609122437
H	9.25883840097572	8.28337266736096	5.56105452055386
H	9.40863144391186	6.71473000966104	4.76178882618697
H	6.52632986280139	7.06404641638822	7.36901593815823
H	7.97001554600186	8.05466536296068	7.34757010159930
H	9.66758630081919	4.72259606618670	7.25109860455654
H	7.67271241326755	5.19298409777641	4.84530111857430
H	6.14432557248250	5.59081805793478	5.63161623454490
H	6.98502925050393	6.52740076847271	2.83833453275590
H	5.82626966664619	5.24271518624255	3.20128695935275
H	3.79090889564645	5.70873031933723	4.17910040965144
H	3.14033507742623	7.33979766845265	3.99516437370797
H	5.81080370699523	8.08184763190614	1.86347475580325
H	4.16630540058735	7.38174626271504	1.80169431383252
H	7.98546319750357	11.00800113072863	4.55141593058015

H	5.73977473035046	9.59903527367996	7.72760329019923
H	6.87146834436561	11.25497131102151	9.26336236116864
H	9.10581518789174	12.67300065609841	6.08015345588090
H	5.98393002080030	14.26542557595597	8.92998285824807
H	6.26154716171624	15.66830833858690	9.97076753057003
H	8.59500344692777	15.33688721071179	6.85364124692125
H	7.09604321339540	14.45400667891272	6.96991408120859
H	6.04287711036681	18.07569062078912	7.71295850321535
H	8.20024052589510	16.91281258778146	9.72266651562466
H	9.49335051447299	16.38562443365312	8.64015458627608
H	8.88877237872105	15.16351395783502	11.38092304580694
H	10.21082330066786	16.28244921945314	11.01672975591327
H	11.94397041546155	15.67270275099092	9.64685558753017
H	12.30576401361278	13.95069895341560	9.48926302632711
H	9.86175115833979	13.26801544367501	11.88628232493109
H	11.58930042176610	13.73872879541178	11.82482906048919

Ru^{III}–Ru^{III}

Ru	6.35313631586340	8.66391131267241	4.95145989651518
N	7.39842729655714	6.82548043660850	5.43563403892326
C	8.75459509343066	6.95822006770035	4.84774447991772
C	8.78886011732661	7.86895701430347	3.61811168876919
O	9.65447178707937	7.73880381469674	2.78938746783295
O	7.85616544116640	8.77679150969179	3.61162102685183
C	7.45000301195156	6.60806277494058	6.88958614434178
C	8.14527767657485	5.37125889484310	7.42386757096349
O	8.34845281290625	5.21299657789065	8.59165089244906
O	8.49405228825157	4.47986777451482	6.48700429843910
C	6.58178456139145	5.78257051450832	4.74304676860877
C	6.00867213758379	6.29347826047418	3.43107520127116
C	3.94126908960143	7.24138928491535	4.38814438021103
N	5.21517116449464	7.51216943515382	3.67710199797245
C	4.08637436135169	7.31607350030394	5.90981386768589
O	3.39895655325220	6.65028711025013	6.63977327074851
O	4.99809523981934	8.17258516399448	6.31381169020809
C	5.01914227135413	8.39422258411945	2.50761416273430
C	4.79722492538568	9.84456031505731	2.97311796961954
O	4.14572376864559	10.60943195093889	2.31589567081081
O	5.41339934153184	10.15735054223894	4.09763150722224
N	7.30583750942130	9.96708020831769	6.21002046593894
C	8.15913905843690	10.87245583871961	5.70915633206999
C	6.97275893604316	10.05832458368358	7.50627391626740
N	8.34421256524656	11.96724143196993	7.80539372955484
C	7.50086752752226	11.05324015439830	8.30866983205702
C	8.67711386391494	11.87627503419798	6.50897309846132
Ru	9.24984506892566	13.36204764187668	9.00985037243418
N	7.82731328310871	14.98502573301259	8.79166189973958
C	6.62549705205350	14.60112857178103	9.57083479216053
C	6.93961316654269	13.65082640937407	10.72771484643521
O	6.20298798584021	13.58802995009184	11.68007212932098
O	8.00107185187388	12.92358565698417	10.53305531986768
C	7.50713872793376	15.21966402318883	7.37430565179121
C	6.50450664222360	16.30128208072120	7.02372673405015
O	6.03946345044000	16.40826799600355	5.92746609011551
O	6.20401829677506	17.12722030480898	8.03566157887037
C	8.54848342483577	16.14054759337945	9.40780503841948
C	9.39001475320030	15.70886503209213	10.59847141930972
C	11.43057346103375	15.17993817009297	9.31724937888094
N	10.34003082688422	14.66111714581060	10.18013447316386
C	11.08140392638884	15.13414899062165	7.82783703248175
O	11.54384410940587	15.92639070017161	7.04912960970171
O	10.26813519002770	14.15296118763271	7.50339423698572
C	10.85758416844812	13.79310869960438	11.25772063602942
C	11.28587201475845	12.43728375396283	10.66721408508022
O	12.16285810715034	11.79200400375535	11.17386091745543
O	10.58544888068887	12.05737966931832	9.61576072880135
H	9.39729711537181	7.42810546485601	5.59715317256758
H	9.17724273061605	5.98215987731220	4.60763022301393
H	6.42927988740467	6.60717613049004	7.28074966567713
H	7.95441612100675	7.46022025521947	7.34752744490607
H	8.92261448555191	3.73898139045422	6.93661745234744
H	7.18508573104398	4.88968350195620	4.57083812062781
H	5.77231995541869	5.50054623004714	5.42143620237592

H	6.80590768823180	6.55198944832201	2.73242862286845
H	5.39638047797343	5.51078735412384	2.96881695465027
H	3.52474206566199	6.27426108088059	4.09832446584162
H	3.22228372269699	8.01459697110592	4.10507200337544
H	5.94024931598064	8.38672883738720	1.92022839121457
H	4.18415705478777	8.07163139778023	1.88150452648369
H	8.40876992060560	10.77798117464341	4.65884913061838
H	6.25261230543414	9.33820882765822	7.87763421045214
H	7.26631344577586	11.13533275774318	9.36339282057800
H	9.37214281603583	12.61823061140849	6.13208119549657
H	5.95107790594276	14.05984633528469	8.90154612697745
H	6.09582837202850	15.48125160164179	9.93686078807172
H	8.43475979456066	15.43423752343946	6.83740316733671
H	7.11780103619230	14.29311664480847	6.95027564730089
H	5.56750577118262	17.77392063111738	7.70207814689897
H	7.83398634778976	16.90871334113968	9.70776262770173
H	9.18633210909041	16.57573879120138	8.63451105679876
H	8.76256867840909	15.29344799187497	11.38894463548687
H	9.91680744695859	16.57747222414387	11.00981413907221
H	11.71351929460905	16.19515713146003	9.60408548384691
H	12.30545951068676	14.53857445069909	9.45173416683208
H	10.04034511825685	13.59563337274498	11.95543798023714
H	11.69385467004880	14.25067924366372	11.79133309280088