Supplementary Material (ESI) for Dalton Transactions

COMPARATIVE SPECTROSCOPIC AND MECHANISTIC STUDY OF CHELATION PROPERTIES OF FISETIN WITH IRON IN AQUEOUS BUFFERED SOLUTIONS. IMPLICATIONS ON *in vitro* ANTIOXIDANT ACTIVITY

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Supplementary Information

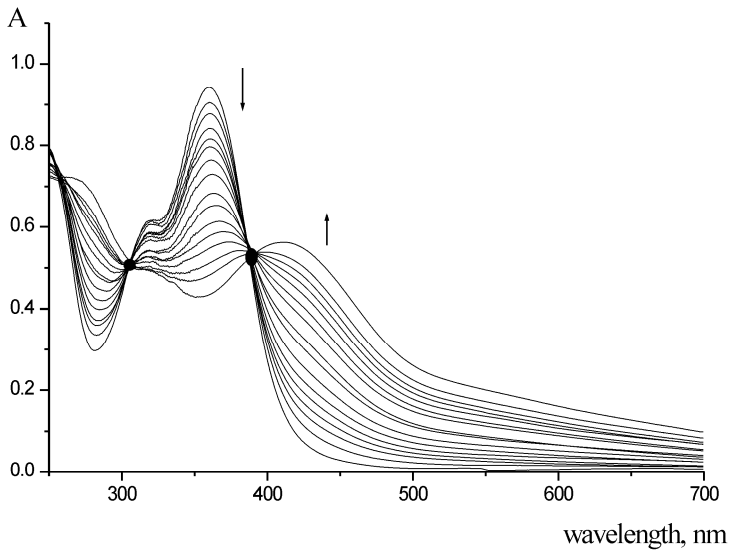
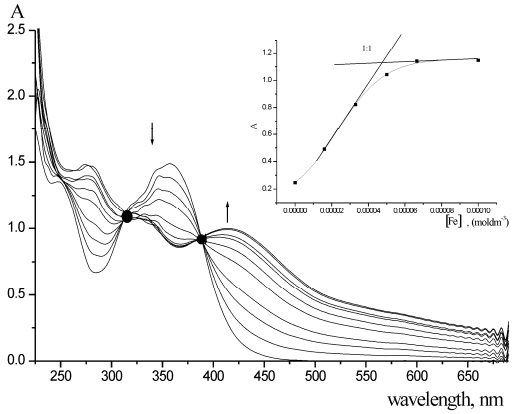


Fig. S1 Titration curves of fisetin with iron at pH 7 acetate buffer



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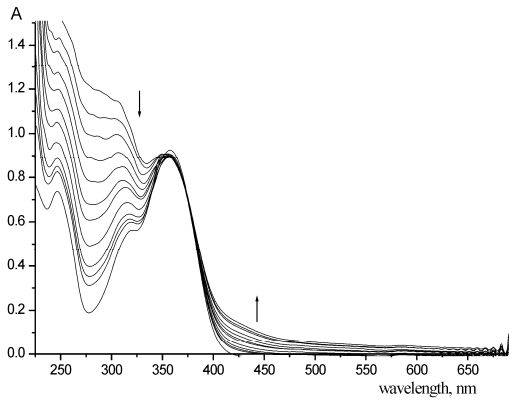

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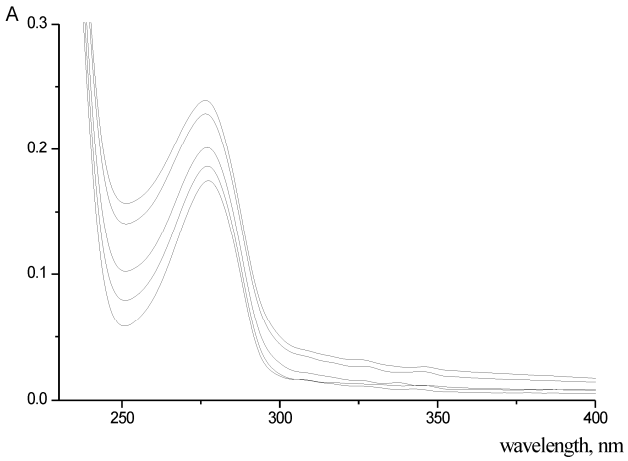


c)

Fig. S2 Titration curves of fisetin with iron at pH 9 phosphate buffer. Inset: complex absorbance at 420 nm *versus* [Fe] concentration (a) titration curves of fisetin with iron at pH 4 phosphate buffer (b) titration curves of catechin with iron at pH 4 acetate buffer (c)

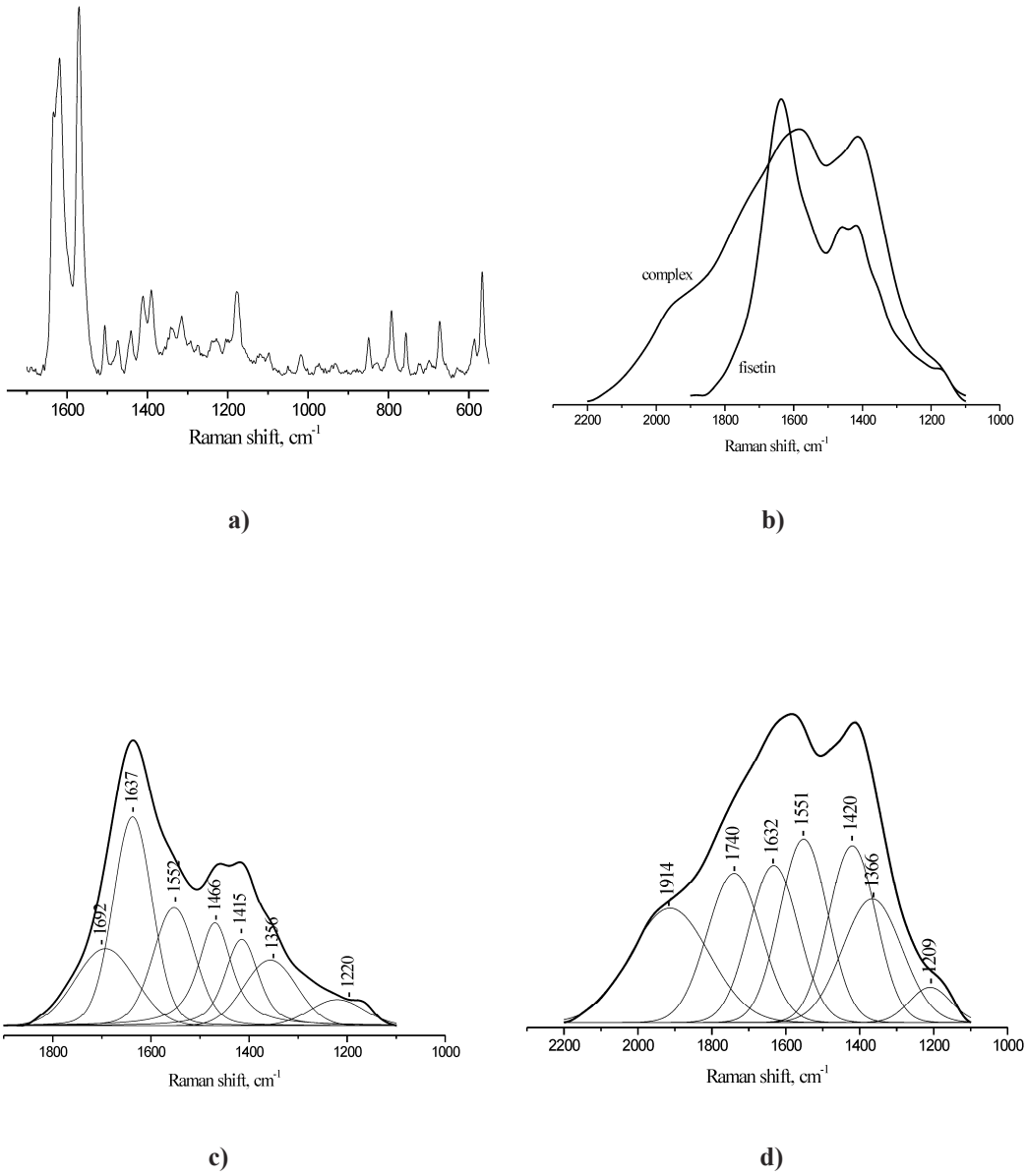


Fig. S3 Raman spectrum of solid fisetin (a) Raman spectra of fisetin and iron-fisetin complex at pH 9 acetate buffer (b) curve fitting analysis of the 1900-1000 cm^{-1} Raman region of fisetin spectrum at pH 9 (c) curve fitting analysis of the 2200-1000cm^{-1} Raman region of iron-fisetin complex spectrum at pH 9 (d)

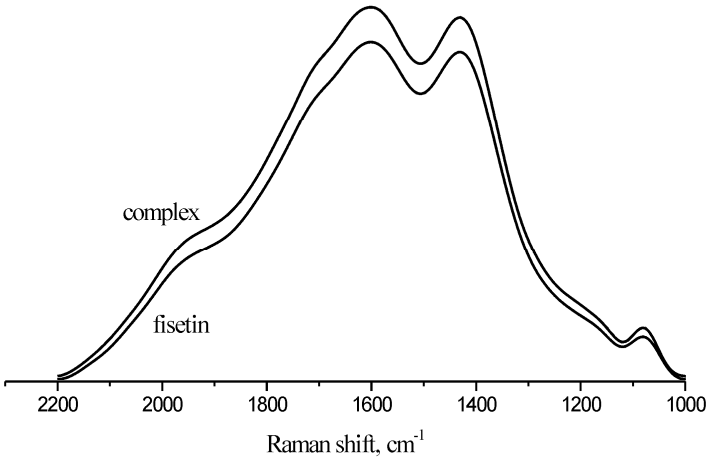
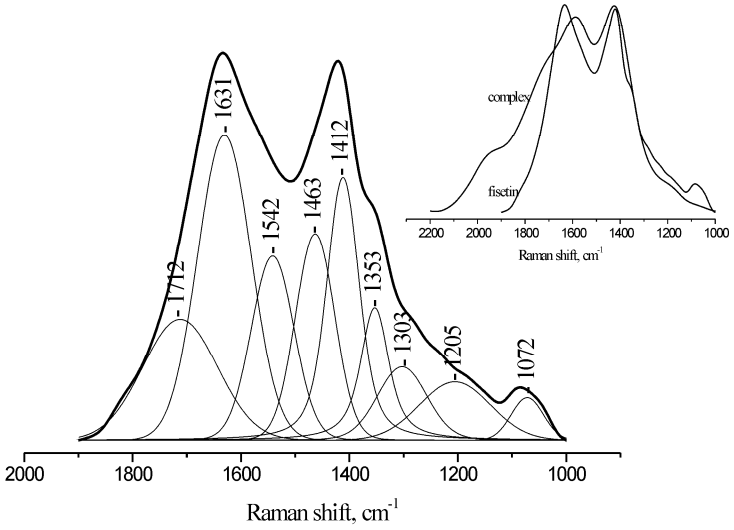


Fig.S4 Raman spectra of fisetin and iron-fisetin complex at pH 4 phosphate buffer



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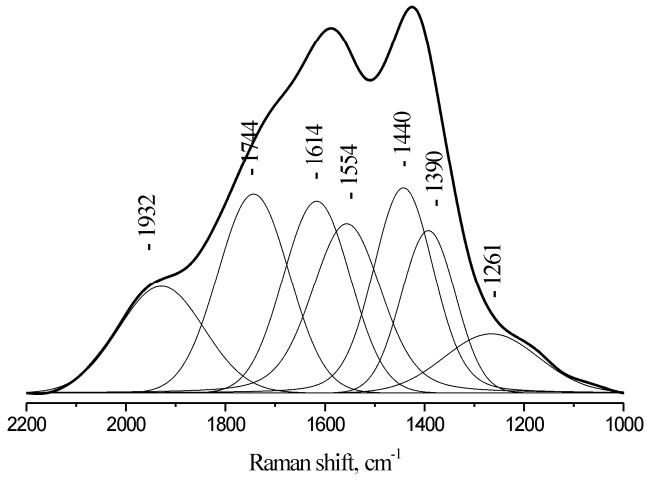
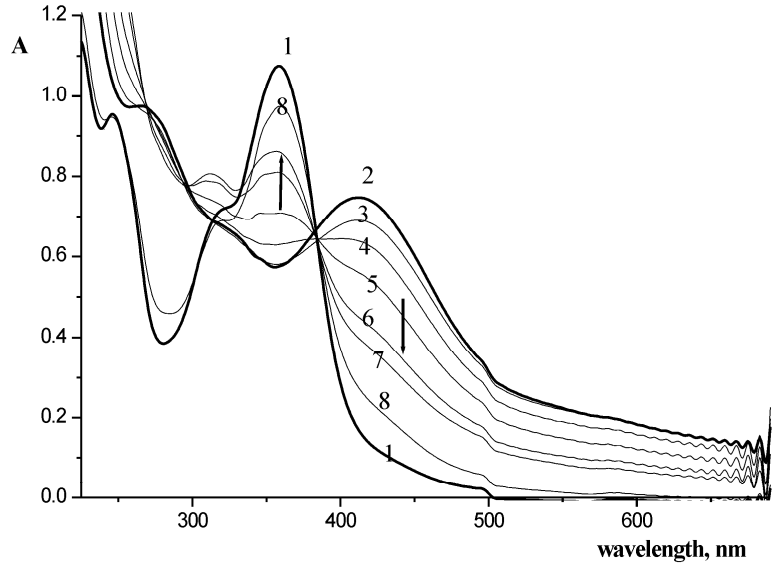


b)

Fig. S5 Curve fitting analysis of the 2000-1000 cm^{-1} Raman region of fisetin spectrum at pH 7. Inset: Raman spectra of fisetin and iron-fisetin complex at pH 7 phosphate buffer (a) curve fitting analysis of the 2200-1000cm^{-1} Raman region of iron-fisetin complex spectrum at pH 7 (b)



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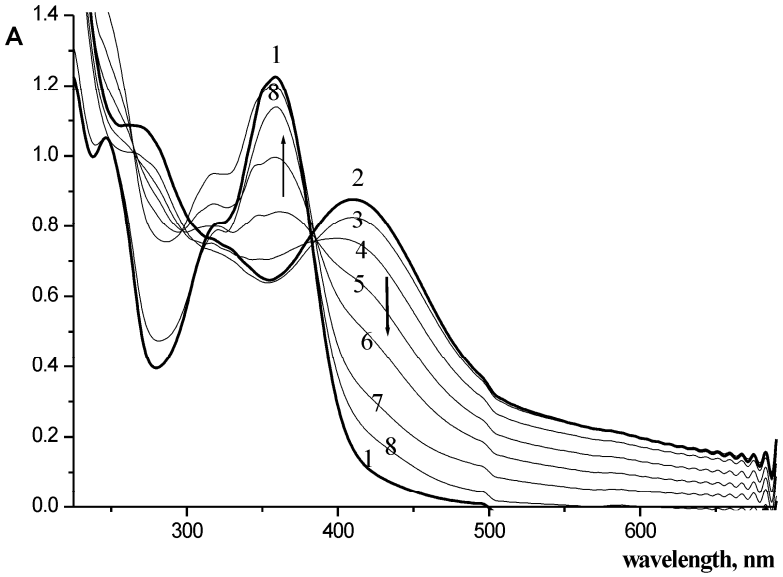
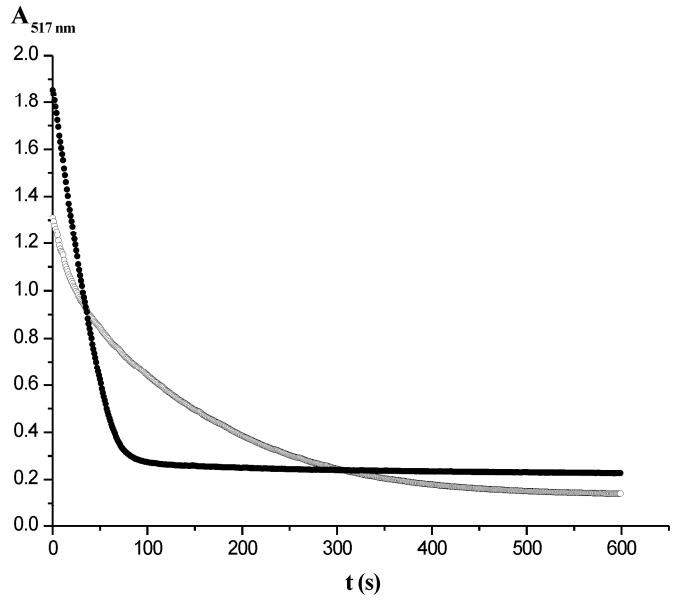
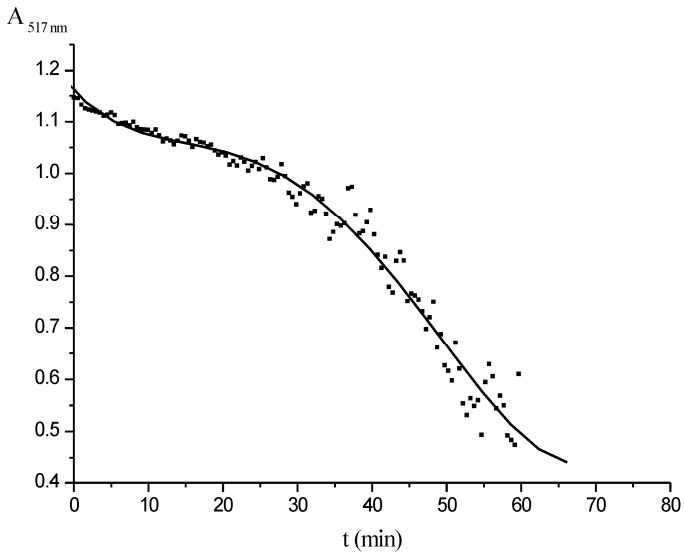


b)

Fig. S6 Iron recovery from iron-fisetin complex (pH 7) by EDTA (a) (1-fisetin; 2: complex; 3: 0.3 mM EDTA ; 4: 1.5 mM EDTA; 5: 3.1 mM EDTA 6: 4.8 mM EDTA 7:6.5 mM EDTA 8: 11.5mM EDTA; and citric acid (b) (1-fisetin; 2: complex; 3: 0.3 mM citric acid; 4: 1.5 mM citric acid; 5: 3.1 mM citric acid 6: 4.8 mM citric acid 7:6.5 mM citric acid 8: 8.1 mM citric acid)



a)



b)

Fig. S7 Deacay of DPPH ($1.5x10^{-4}$ $moldm^{-3}$) visible absorbance at 517 nm by fisetin (○)($5x10^{-5}$ $moldm^{-3}$ in ethanol) and iron-fisetin complex (•) (1:1, in ethanol) (a) and iron-fisetin complex (1:1) in acetate buffer pH 7 (b)

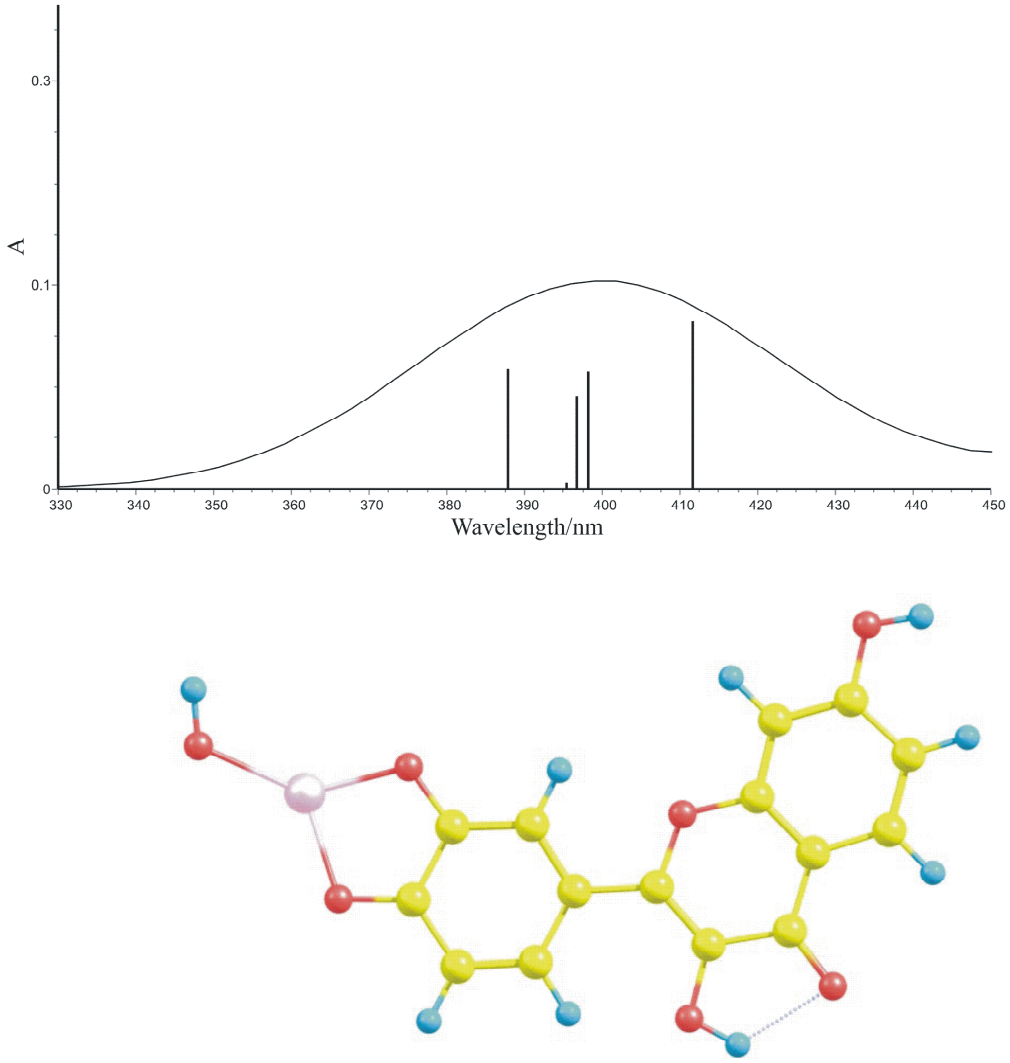


Fig. S8 Geometry optimized structure of the 1:1 iron-fisetin complex and the calculated electronic spectra of the supposed complex structure

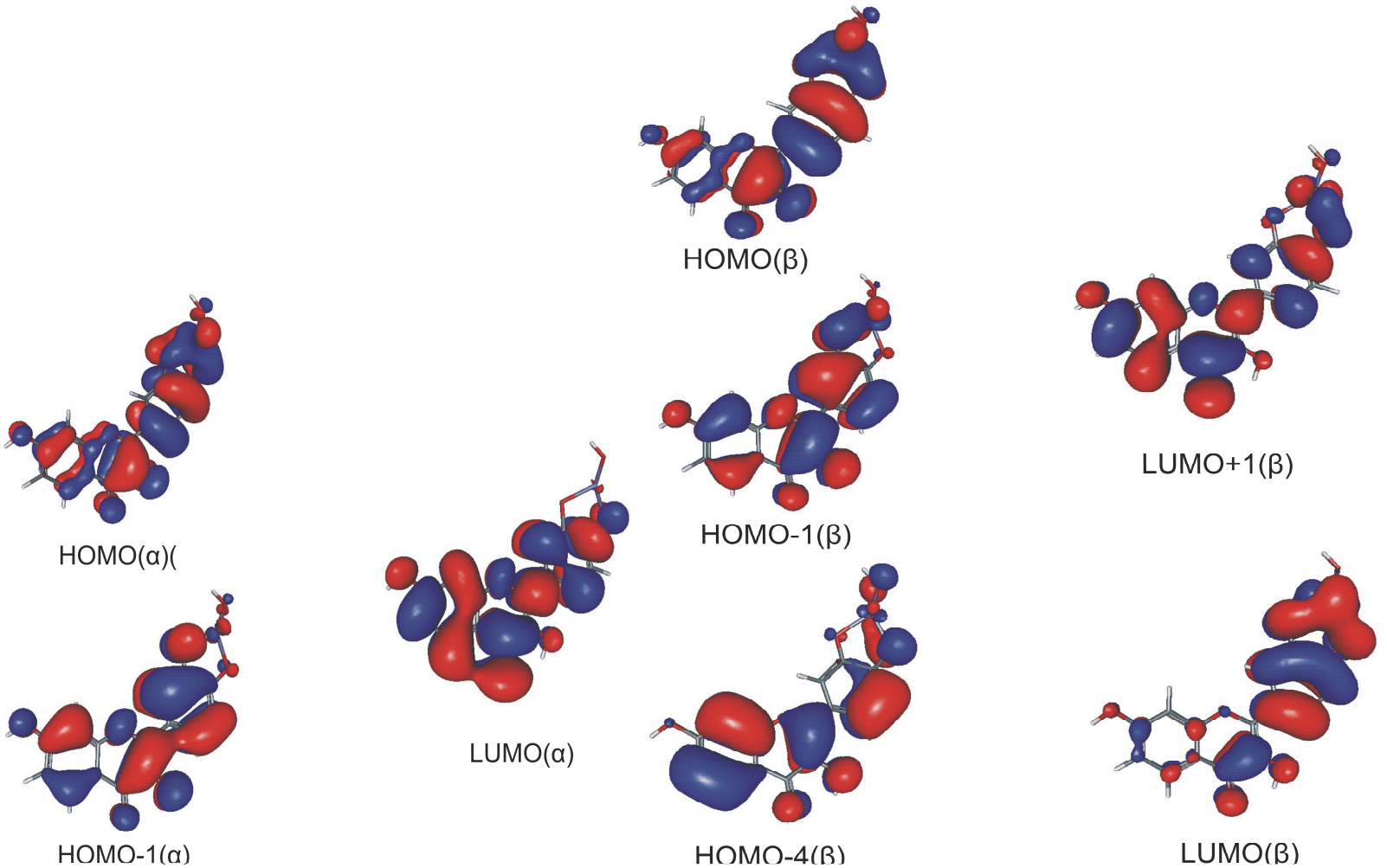


Fig. S9 The corresponding HOMO and LUMO orbitals responsible for UV-spectrum of the 1:1 iron-fisetin complex

1:1 iron-fisetin complex

E=-3474.02053976 Hartree

0 6

H	0.53207200	-1.20313000	0.01252000
O	3.17339100	-1.27659500	0.07567100
H	-2.58298400	3.70091300	-0.00772900
O	-4.27572200	2.67169500	-0.00765800
Fe	5.11964100	-0.84690800	-0.18544000
O	6.73604200	-1.65041000	0.26748200
H	6.77960700	-2.61007600	0.32019300
O	-1.72913600	3.22138800	-0.00788400
C	-3.52094200	1.68154400	-0.00621000
C	-5.29558900	-0.09466100	-0.00063100
H	-6.68624600	-1.72497500	0.00496400
C	1.02343000	-0.24044100	0.01736500
C	2.42675400	-0.21090400	0.04218400
C	-2.07954800	1.91494300	-0.00618100
C	-3.94277100	0.29900600	-0.00305100
C	-5.64366000	-1.42717000	0.00280600
C	-1.17224300	0.88622600	-0.00205100
C	-2.96047200	-0.70392000	-0.00164800
C	-4.63296800	-2.41344100	0.00385800
C	0.28635300	0.94588800	0.00784600
O	-1.63668600	-0.40403600	-0.00231600
C	-3.29081300	-2.05757700	0.00134600
H	-5.87875200	-3.87826900	0.01046100
O	4.41475300	1.03775700	0.10084600
C	3.12293700	1.07084300	0.05424500
O	-4.92330400	-3.73942600	0.00761200
H	-2.51556700	-2.81243600	0.00259000
C	0.98176000	2.19977700	0.01472600
C	2.35483900	2.25986600	0.03562400
H	0.41450400	3.11706800	0.00557300
H	2.86828700	3.21421200	0.04280400
H	-6.05870200	0.67343700	-0.00132100

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13 25 1.0

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29 31 1.0

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cis 1:2 iron-fisetin complex

E=-3474.02013920 Hartree

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C	1.68238910	-0.00867353	0.92294121
H	1.43586229	-0.01742571	4.31900248
C	1.87317586	-0.01605075	3.32838039
H	1.28113888	0.46429974	12.58015633
H	2.17511526	0.29772965	10.26518960
C	3.06019014	-0.01967238	0.78483642
H	1.84053772	0.67704983	14.78956866
C	2.35060552	0.49504697	12.39628452
H	3.51819452	-0.02162338	-0.19532307
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C	2.84099502	0.40396239	11.11252806
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O	3.74902890	-0.03192747	5.55359791
C	3.24418661	0.62550829	13.48177142
C	4.15987777	-0.03529258	4.35812193
O	4.11573062	0.24055775	8.49875229
C	4.22891725	0.44091407	10.86865623
O	5.18581550	-0.04372497	1.76523318
C	4.80628862	0.34929477	9.55515366
C	4.61324913	0.66214651	13.27497694
H	6.19712477	-2.01273546	7.69209301
H	6.08530265	-1.97854487	6.16472466
O	5.55002426	-1.94527609	6.97613828
H	4.51006269	2.51513742	7.22545001
Fe	5.23657584	0.09486574	6.85804920
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O	5.20459195	2.14240152	6.66793329
C	5.59597580	-0.06036823	4.13050483
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H	5.29627483	0.75986563	14.10828523
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C	6.25342538	0.38359196	9.41904956
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C	7.45936871	-0.09088703	2.38363259
C	7.76068466	-0.13423834	1.00684994
C	7.03171480	0.51482827	10.56330456
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C	8.52376439	-0.07312422	3.30578154
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O	9.33320355	-0.20395667	-0.77472314
C	8.48634025	0.57746781	10.64631196
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C	9.11602057	0.70949282	11.90143391
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H	10.65671457	-0.08229966	3.57101046
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C	10.49479043	0.77111528	12.00286232
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60 63 1.5 64 1.0

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63 66 1.0

64 65 1.0

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66 67 1.0

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trans 1:2 iron-fisetin complex

E=-3474.02053976 Hartree

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H	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	0.96564022
H	0.18596521	0.00000000	6.81918070
H	-0.58701099	0.43809937	3.43977034
O	0.46969163	-0.19469007	9.37720790
C	-1.04574200	0.76623023	1.39623982
H	0.38841203	-0.13336404	10.33476567
O	-1.60248063	1.16639844	-0.85130753
C	-1.26253483	0.92855364	2.75341139
C	-0.56858958	0.51888696	7.39528654
H	-2.22674866	1.63074190	-1.41751452
C	-1.89987967	1.38847105	0.47480987
C	-0.54015411	0.50055807	8.77938519
O	-1.58749528	1.21812501	5.40786711
C	-1.59159763	1.22263574	6.75456684
C	-2.33463454	1.71281251	3.22783566
C	-2.95889021	2.16444047	0.92641151
C	-1.52288802	1.17918808	9.53297569
H	-1.48100128	1.15530919	10.61758328
C	-2.54464849	1.87394057	4.66146211
C	-3.18396505	2.33153092	2.28945915
H	-3.61717479	2.64536284	0.20832795
C	-2.58413884	1.90533874	7.47984781
C	-2.52543035	1.86886841	8.88805078
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H	-4.00624887	2.93588506	2.64145866
C	-3.60050314	2.60757839	6.74535529
H	-3.28730791	2.39932720	9.44549274
O	-4.53002659	3.22180210	4.68284355
O	-4.54391493	3.24634857	7.30299882
O	-4.34006900	5.81757664	6.10462440
H	-4.41797860	6.34681555	5.30094549
H	-4.76195429	6.32440603	6.81534737
Fe	-5.64906105	4.23935750	5.97789324
H	-6.53617148	2.15431166	5.14043545
H	-6.88013602	2.13189634	6.65483917
O	-6.95805283	2.66113817	5.85116302

O	-6.75420643	5.23236587	4.65278733
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C	-8.96348710	6.76590586	8.72794925
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H	-9.07138057	6.84797214	13.37329866
C	-10.72953188	7.95982751	4.56049645
C	-10.03558483	7.55016696	9.20237128
O	-9.69564083	7.31232602	12.80709154
H	-11.68653365	8.61207615	1.62101794
C	-10.25237856	7.71249231	10.55954352
O	-11.76781293	8.67340317	2.57857477
H	-10.71110866	8.04062123	8.51601232
H	-11.48408623	8.47871664	5.13660262
O	-11.29812024	8.47872353	10.99014217
H	-11.29812112	8.47872292	11.95578146

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66 67 1.0

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Table 1 Vibrational frequencies of fisetin-iron complexes

1:1 iron-fisetin complex		*trans* 1:2 iron-fisetin complex		*cis* 1:2 iron-fisetin complex	
Freq. (cm^{-1})	IR intensity	Freq. (cm^{-1})	IR intensity	Freq. (cm^{-1})	IR intensity
35.13	0.16	10.81	0.02	10.42	0.02
60.85	0.22	14.62	0.02	14.66	0.02
65.53	0.50	21.94	0.03	21.57	0.03
84.37	0.22			27.82	0.02
91.49	4.67	32.85	3.43	31.37	2.16
113.61	3.08			42.74	1.77
118.48	2.34			43.87	0.08
129.00	14.43	54.35	3.10	62.03	1.04
157.92	13.84			65.22	1.53
186.89	2.53			68.80	3.86
201.98	249.77	84.93	3.26	72.37	0.53
213.93	12.19	95.50	0.19	95.21	5.92
229.56	3.06			101.07	2.49
255.15	2.29			110.76	4.03
277.84	21.87	121.23	0.33	116.06	3.77
292.20	1.27			121.56	0.34
316.41	11.87			127.82	1.34
344.84	6.24	137.86	1.81	138.29	3.13
352.95	88.47	156.82	44.13	139.84	14.06
362.43	4.77			158.42	25.75
381.14	161.23			181.42	4.84
396.31	17.59	197.29	40.30	197.54	11.38
404.10	4.23	204.07	17.85	206.45	34.12
442.53	0.80			208.17	19.72
450.22	0.37	212.80	25.29	216.14	1.28
467.49	1.59	234.17	111.48	229.35	62.39
511.29	6.77			234.69	1.83
542.80	15.32	236.74	3.10	236.88	53.89
549.72	2.77	244.28	208.94	245.35	189.09
564.95	23.22			252.21	3.21
608.97	96.54			256.76	7.98
613.43	117.23			259.77	2.50
622.03	70.54	267.29	4.05	262.77	16.92
636.11	2.80	269.82	3.42	266.94	3.28
644.71	266.44			273.40	6.86
652.06	306.12			303.32	4.17
660.99	0.84	310.98	11.54	310.36	12.33
680.43	12.28	318.57	60.56	310.58	5.48
680.65	37.54	322.17	32.74	311.43	25.08
703.02	14.79			317.34	17.90
709.75	7.64	336.85	34.05	332.20	16.06
729.33	36.09			345.59	0.63
732.82	234.88	348.81	16.60	346.29	0.08
769.24	1.25			351.24	2.36
820.34	181.94	361.30	0.13	364.86	101.74
821.01	27.14	361.51	225.79	368.88	122.01
825.60	34.22			386.02	9.49
848.21	39.69			387.43	11.38
858.93	37.32	402.54	49.01	409.06	2.04
881.59	32.17			412.21	16.57

944.95	0.94	419.65	85.21	418.68	55.01
956.69	6.33			421.73	3.19
971.78	0.85	424.56	12.65	422.75	63.38
980.84	42.78	429.60	121.26	436.55	96.38
1038.66	51.78	445.89	37.20	438.60	40.98
1118.72	32.12			452.68	0.61
1146.53	407.59	452.35	5.44	452.93	6.28
1149.49	32.03			461.85	6.31
1179.25	265.75			466.56	0.39
1202.51	412.57	467.60	2.23	467.31	0.39
1227.00	54.00	468.88	2.40	469.17	3.16
1242.15	33.55			491.17	5.62
1252.56	58.10	496.44	5.69	494.80	4.23
1281.17	1.42			514.87	51.95
1296.72	633.22	519.79	55.59	522.18	3.69
1315.31	567.09			543.34	23.84
1336.15	22.53	547.72	8.15	546.42	2.81
1349.47	157.63			548.21	0.60
1357.90	469.16	553.79	21.77	551.49	10.63
1411.92	72.25			578.21	226.48
1435.99	936.26	588.91	68.93	587.91	13.85
1462.90	106.38			589.08	55.00
1494.89	18.61	597.61	2.99	597.15	0.99
1500.49	409.90			598.00	1.83
1546.95	160.18			629.08	29.63
1592.54	2.05	632.30	64.66	632.66	2.90
1610.33	171.25	633.21	300.38	633.71	7.79
1625.52	94.92			637.66	10.63
1647.04	1001.60			642.37	67.93
1668.78	524.02	645.47	303.32	651.54	0.89
1684.18	33.44	652.51	6.03	652.60	0.38
3194.10	14.13			666.37	10.99
3199.13	23.83	674.06	5.85	672.46	82.93
3220.66	9.70			676.69	27.43
3229.80	1.90			684.13	17.17
3231.88	1.65	685.30	187.65	688.07	148.54
3261.35	4.52	690.07	69.14	694.75	0.75
3521.44	307.27	695.26	1.46	695.43	0.06
3802.13	202.23			701.30	15.38
3840.04	291.33			704.45	191.26
		706.96	24.28	708.08	122.00
				725.89	22.41
		727.94	31.42	727.88	28.64
				769.21	0.63
		769.28	0.48	769.58	0.41
		801.25	156.24	801.20	65.50
		801.61	0.00	801.78	78.13
		804.80	0.00	804.50	22.54
		804.89	47.07	806.13	30.89
		810.55	55.27	808.45	1.32
				809.93	50.63
		852.78	0.18	852.06	22.24
		852.82	48.08	852.46	26.69
				853.42	24.10
		855.92	34.68	856.43	1.64
				887.99	15.25
		887.28	36.07	888.75	20.68
		938.19	0.40	932.54	0.01

				934.24	0.13
		959.12	3.10	959.16	0.95
				959.69	2.11
				967.33	23.07
		970.40	28.80	970.60	10.63
				985.68	4.60
		985.42	29.46	985.84	25.38
				1048.94	39.21
		1049.71	73.30	1050.03	24.49
		1130.76	0.03	1130.28	19.45
		1130.78	113.81	1130.77	81.84
		1136.51	0.00	1136.84	9.41
		1136.88	374.46	1137.51	370.81
		1163.45	56.92	1162.47	56.58
				1163.71	31.21
		1180.21	155.06	1178.58	83.46
				1180.26	55.03
		1186.20	452.78	1186.37	254.92
				1187.02	226.68
		1217.88	886.81	1216.10	970.74
				1220.09	5.35
		1228.09	2.42	1227.10	0.41
				1228.13	0.27
				1243.30	10.62
		1243.61	9.43	1244.07	7.27
		1254.97	486.20	1253.67	449.31
				1258.05	0.50
		1289.33	69.88	1288.52	20.12
				1290.64	29.58
				1320.58	46.03
		1321.18	542.67	1321.24	467.50
		1338.29	311.58	1338.29	256.29
				1338.93	76.29
		1354.00	646.29	1352.48	555.96
				1354.11	82.78
				1359.14	43.75
		1359.59	66.81	1359.48	28.66
		1388.43	137.15	1388.24	63.42
				1388.99	90.29
		1410.99	225.92	1410.81	152.29
				1412.12	9.31
		1439.98	994.09	1438.00	376.17
				1443.16	480.16
				1494.53	11.61
		1495.18	45.63	1495.79	27.84
		1502.77	0.41	1503.19	184.95
		1502.78	432.17	1504.96	251.61
				1545.42	80.69
		1546.78	255.45	1548.77	78.56
		1556.22	582.36	1556.54	201.15
				1557.44	335.33
				1567.69	29.40
		1567.35	223.20	1573.78	153.17
		1580.79	670.99	1580.90	398.69
		1585.40	0.00	1593.00	206.13
		1625.85	442.12	1626.71	226.79
				1629.05	148.15
		1632.48	23.36	1630.33	33.63

				1644.86	33.57
				1646.19	22.50
		1645.22	53.22	1672.00	22.24
		1672.31	0.08	1672.71	30.13
		1672.33	51.88	1676.72	43.29
		1680.41	486.94	1680.09	264.12
				1681.03	241.92
		3165.61	56.18	3163.89	25.18
				3166.50	26.29
		3173.51	45.39	3173.21	24.15
				3174.92	23.19
		3222.23	4.97	3222.35	2.17
		3222.24	0.03	3222.67	2.88
		3234.63	1.44	3234.35	1.20
		3234.64	0.74	3234.66	1.14
		3243.53	3.71	3244.31	1.70
		3243.53	0.01	3244.49	1.69
		3255.00	24.09	3254.48	8.85
		3255.03	0.56	3255.51	10.60
				3597.25	209.94
		3637.06	372.94	3737.95	42.40
		3788.40	216.12	3776.29	124.52
		3788.45	6.22	3787.96	99.44
		3823.86	194.65	3788.66	112.02
		3823.91	0.73	3823.10	99.52
		3829.61	0.02	3823.68	110.85
		3830.05	101.02	3839.73	74.02
		3839.96	202.48	3841.09	104.68
		3840.01	0.31	3846.25	52.66