Electronic Supporting Information

Syntheses, Characterization, Electrochemical and Spectroscopic Properties of Ruthenium-Iron Complexes of 2,3,5,6-Tetrakis(2-pyridyl)pyrazine and Ferrocene-Acetylide Ligands

Hui-Min Wen, Jin-Yun Wang,* Li-Yi Zhang, Lin-Xi Shi, and Zhong-Ning Chen*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Table S1. Selected bond lengths (Å) and bond angles (˚) of complex $[\mathbf{1}]^+$ in ground state by DFT method at the PBE1PBE and B3LYP levels, compared with the experimentally measured data.

Parameters	B3LYP	PBE1PBE	X-ray Crystallography[a]
bond distance (Å)			
Ru1-N1	2.1205	2.0890	2.087(3)
Ru1-N2	2.0200	1.9964	1.983(3)
Ru1-N3	2.1178	2.0871	2.092(4)
Ru1-P1	2.5446	2.4750	2.4026(12)
Ru1-P2	2.5346	2.4676	2.4009(12)
Ru1-C61	2.0469	2.0276	2.071(3)
C61-C62	1.2342	1.2343	1.198(4)
C62-C63	1.4244	1.4218	1.425(5)
bond angle (˚)			
P1-Ru1-P2	175.397	175.884	173.52(4)
P1-Ru1-N1	91.338	91.760	92.07(10)
P2-Ru1-N1	89.006	88.393	88.82(14)
P1-Ru1-N2	92.148	92.008	93.47(10
P1-Ru1-N3	89.247	88.611	88.87(10)
P2-Ru1-N2	92.417	92.055	91.44(10)
P2-Ru1-N3	92.249	92.817	87.91(10)
N2-Ru1-N1	78.306	78.738	78.43(13)
N2-Ru1-N3	78.432	78.841	78.95(14)
N1-Ru1-N3	156.736	157.575	157.37(14)
Ru1-C61-C62	177.779	177.783	170.0(4)
C61-C62-C63	175.697	175.912	174.3(6)

[a] The experimental values from X-ray crystal structural analysis.

Table S2. Geometry coordinates of optimized complex $[\mathbf{1}]^+$ by DFT method at the PBE1PBE level.

center number	atomic type	coordinates (Angstroms)		
		X	Y	Z
1	Ru	-0.008295	0.198995	0.011991
2	Fe	6.278894	0.031177	-0.035873
3	P	0.513812	-2.159430	0.516000
4	P	-0.360980	2.602221	-0.463014
5	N	-0.312085	-0.194141	-2.015061
6	N	-1.970513	-0.167474	-0.020674
7	N	-0.505225	0.457754	2.024468
8	N	-4.614236	-0.680625	-0.064414
9	N	-3.877675	-2.695376	-2.803441
10	N	-4.771357	1.449151	2.678657
11	C	0.593214	-0.095631	-2.996754
12	H	1.609433	0.085091	-2.669166
13	C	0.258808	-0.193863	-4.338955
14	H	1.032123	-0.101011	-5.093425
15	C	-1.074571	-0.385781	-4.680753
16	H	-1.380734	-0.437230	-5.720714
17	C	-2.016543	-0.511385	-3.670187
18	H	-3.060180	-0.655320	-3.911111
19	C	-1.615730	-0.442475	-2.335913
20	C	-2.535107	-0.538075	-1.188487
21	C	-3.881283	-0.953022	-1.142392
22	C	-4.071224	-0.162643	1.034999
23	C	-2.669296	-0.044869	1.126227
24	C	-1.817967	0.203730	2.302267
25	C	-2.260100	0.123908	3.622750
26	H	-3.288472	-0.134901	3.830692
27	C	-1.376063	0.370854	4.662912
28	H	-1.714822	0.309691	5.692190
29	C	-0.059711	0.700402	4.363901
30	H	0.663688	0.919154	5.141443
31	C	0.333188	0.723174	3.034127
32	H	1.350685	0.946663	2.741616
33	C	-4.584154	-1.738808	-2.186975

34	C	-5.940857	-1.513240	-2.431960
35	H	-6.460291	-0.732121	-1.888500
36	C	-6.584552	-2.309869	-3.371386
37	H	-7.636176	-2.156991	-3.594854
38	C	-5.858775	-3.305284	-4.016784
39	H	-6.320965	-3.953442	-4.754082
40	C	-4.511778	-3.457818	-3.692680
41	H	-3.913723	-4.231003	-4.170749
42	C	-5.049268	0.298630	2.051788
43	C	-6.229285	-0.419012	2.260860
44	H	-6.402459	-1.337178	1.711043
45	C	-7.152313	0.077778	3.173629
46	H	-8.076397	-0.458184	3.368705
47	C	-6.872274	1.271940	3.828860
48	H	-7.565707	1.699035	4.545858
49	C	-5.671058	1.918038	3.541756
50	H	-5.420361	2.858284	4.028710
51	C	1.287736	-3.139168	-0.881366
52	C	0.929447	-4.455722	-1.175277
53	H	0.134526	-4.946903	-0.623062
54	C	1.598623	-5.152262	-2.179239
55	H	1.313460	-6.176139	-2.402926
56	C	2.633228	-4.544911	-2.884375
57	H	3.154907	-5.091856	-3.664225
58	C	3.005928	-3.239234	-2.575884
59	H	3.823143	-2.765292	-3.112498
60	C	2.339402	-2.535682	-1.576272
61	H	2.647343	-1.526404	-1.311854
62	C	1.671883	-2.601320	1.927826
63	C	2.590732	-1.675580	2.420309
64	H	2.652663	-0.690425	1.969485
65	C	3.464887	-2.040180	3.444293
66	H	4.174258	-1.310706	3.825407
67	C	3.438826	-3.328430	3.967295
68	H	4.122207	-3.609442	4.763273
69	C	2.542939	-4.264285	3.453798
70	H	2.529240	-5.278204	3.842568
71	C	1.665926	-3.904971	2.436447

72	H	0.973318	-4.642838	2.041973
73	C	-1.049837	-3.080350	0.975280
74	C	-1.933418	-3.520685	-0.015890
75	H	-1.696172	-3.395855	-1.068626
76	C	-3.138102	-4.125140	0.335470
77	H	-3.805927	-4.469172	-0.448379
78	C	-3.482247	-4.281033	1.675478
79	H	-4.418340	-4.760638	1.946509
80	C	-2.619020	-3.821074	2.666071
81	H	-2.878760	-3.936275	3.714571
82	C	-1.411071	-3.220998	2.319330
83	H	-0.741011	-2.875534	3.100865
84	C	-2.140967	2.895644	-0.958790
85	C	-3.154747	2.969061	0.002390
86	H	-2.923416	2.922989	1.062624
87	C	-4.485893	3.095204	-0.388468
88	H	-5.256636	3.160501	0.373374
89	C	-4.822360	3.130937	-1.738670
90	H	-5.860313	3.237714	-2.040309
91	C	-3.820677	3.029655	-2.700313
92	H	-4.072442	3.053596	-3.756801
93	C	-2.488352	2.910043	-2.314208
94	H	-1.714632	2.843430	-3.073163
95	C	0.584536	3.490413	-1.823102
96	C	1.807219	3.005044	-2.283009
97	H	2.212205	2.091640	-1.860783
98	C	2.530302	3.725480	-3.232861
99	H	3.488834	3.345764	-3.575176
100	C	2.040303	4.930590	-3.723479
101	H	2.606201	5.490752	-4.462109
102	C	0.827726	5.427770	-3.249507
103	H	0.446505	6.377225	-3.613916
104	C	0.105718	4.716441	-2.297857
105	H	-0.831248	5.120427	-1.925345
106	C	-0.010696	3.754726	0.972388
107	C	-0.845490	4.814188	1.329613
108	H	-1.782736	4.979653	0.807956
109	C	-0.470505	5.679516	2.355559

110	H	-1.126038	6.501120	2.629479
111	C	0.742136	5.503319	3.014758
112	H	1.034041	6.184646	3.808556
113	C	1.587157	4.461289	2.640689
114	H	2.546028	4.332674	3.134969
115	C	1.214956	3.587695	1.623591
116	H	1.882804	2.787269	1.311959
117	C	1.986057	0.564710	0.015261
118	C	3.195479	0.807643	-0.025735
119	C	4.565194	1.180045	-0.107153
120	C	5.416419	1.583368	0.977284
121	H	5.141103	1.568260	2.023036
122	C	6.674024	1.975045	0.443507
123	H	7.533170	2.297743	1.015968
124	C	6.625440	1.810485	-0.970057
125	H	7.441327	1.986383	-1.658092
126	C	5.337895	1.315248	-1.311607
127	H	4.993082	1.056261	-2.303680
128	C	6.605383	-1.485008	1.295834
129	H	6.350986	-1.450808	2.346068
130	C	7.835053	-1.057067	0.718270
131	H	8.674565	-0.630790	1.250698
132	C	7.742404	-1.233572	-0.691644
133	H	8.500117	-0.966509	-1.415952
134	C	6.455441	-1.771218	-0.983128
135	H	6.069573	-1.989718	-1.969451
136	C	5.753035	-1.928526	0.245293
137	H	4.737202	-2.281274	0.358919

Table S3. Geometry coordinates of optimized complex [**1a**]$^{2+}$ by DFT method at the PBE1PBE level.

center number	atomic type	coordinates (Angstroms)		
		X	Y	Z
1	Ru	0.000174	0.353749	0.017111
2	Fe	-6.253043	0.080994	-0.037604
3	P	-0.733405	-1.963648	-0.488946
4	P	0.688398	2.675555	0.547578
5	N	0.319106	-0.100887	2.044511
6	N	1.923655	-0.255979	-0.003517
7	N	0.514897	0.635700	-2.003178
8	N	4.462823	-1.124383	-0.035825
9	N	3.441560	-3.114823	2.631223
10	N	4.830385	1.102443	-2.680033
11	C	-0.515969	0.123607	3.066410
12	H	-1.509762	0.450025	2.790387
13	C	-0.143752	-0.023113	4.394396
14	H	-0.862140	0.180771	5.180610
15	C	1.160160	-0.407119	4.680759
16	H	1.499413	-0.506008	5.706833
17	C	2.030054	-0.660210	3.630132
18	H	3.053547	-0.948122	3.825464
19	C	1.587405	-0.525903	2.314932
20	C	2.449985	-0.729482	1.138064
21	C	3.722269	-1.337135	1.047793
22	C	3.982961	-0.495053	-1.104471
23	C	2.601706	-0.198422	-1.161619
24	C	1.772993	0.204869	-2.311591
25	C	2.191673	0.123545	-3.638928
26	H	3.166542	-0.281188	-3.871127
27	C	1.356345	0.565707	-4.654725
28	H	1.677155	0.507334	-5.689779
29	C	0.117597	1.097733	-4.320486
30	H	-0.555377	1.490179	-5.074741
31	C	-0.263685	1.102161	-2.986838
32	H	-1.225547	1.488793	-2.674604
33	C	4.300770	-2.271606	2.042413

34	C	5.678133	-2.296688	2.268566
35	H	6.322606	-1.595570	1.750286
36	C	6.181684	-3.236055	3.162154
37	H	7.245900	-3.280661	3.372538
38	C	5.298843	-4.116750	3.777071
39	H	5.648552	-4.868754	4.476626
40	C	3.941326	-4.017362	3.473546
41	H	3.223583	-4.696159	3.928986
42	C	4.996292	-0.099989	-2.112602
43	C	6.094608	-0.923414	-2.366676
44	H	6.178473	-1.880768	-1.864851
45	C	7.058482	-0.477497	-3.264744
46	H	7.922694	-1.092961	-3.495347
47	C	6.896792	0.769871	-3.857167
48	H	7.626735	1.159620	-4.558928
49	C	5.768525	1.520602	-3.527887
50	H	5.613875	2.504398	-3.965685
51	C	-1.466318	-2.889055	0.967669
52	C	-1.182404	-4.228588	1.239031
53	H	-0.470491	-4.774845	0.628554
54	C	-1.814249	-4.876416	2.299268
55	H	-1.586919	-5.918607	2.502363
56	C	-2.732007	-4.194805	3.092068
57	H	-3.217484	-4.700976	3.920998
58	C	-3.024373	-2.860539	2.816570
59	H	-3.733330	-2.321814	3.440660
60	C	-2.399045	-2.209441	1.756533
61	H	-2.635112	-1.172809	1.529730
62	C	-2.048918	-2.280654	-1.793785
63	C	-2.647111	-1.243527	-2.505773
64	H	-2.397866	-0.219268	-2.263253
65	C	-3.583911	-1.524427	-3.501818
66	H	-4.029187	-0.710084	-4.067393
67	C	-3.938305	-2.841163	-3.779053
68	H	-4.657455	-3.061776	-4.562648
69	C	-3.360735	-3.881250	-3.050397
70	H	-3.636209	-4.911000	-3.257099
71	C	-2.419331	-3.603562	-2.065032

72	H	-1.966842	-4.421637	-1.511980
73	C	0.666201	-3.032980	-1.119056
74	C	1.613689	-3.567243	-0.238759
75	H	1.532011	-3.422404	0.835508
76	C	2.685195	-4.307359	-0.733012
77	H	3.404454	-4.728740	-0.037024
78	C	2.829810	-4.508902	-2.103224
79	H	3.661113	-5.094828	-2.483849
80	C	1.898704	-3.963342	-2.982849
81	H	2.000971	-4.119784	-4.052682
82	C	0.821228	-3.228408	-2.495068
83	H	0.093869	-2.821052	-3.190807
84	C	2.480801	2.711532	1.074884
85	C	3.505596	2.633393	0.125063
86	H	3.286636	2.605059	-0.938833
87	C	4.836665	2.591959	0.532710
88	H	5.618946	2.546473	-0.218740
89	C	5.158614	2.611132	1.887169
90	H	6.197812	2.590639	2.201714
91	C	4.141753	2.663575	2.836513
92	H	4.383324	2.681445	3.895290
93	C	2.809149	2.711206	2.434751
94	H	2.026396	2.766788	3.185161
95	C	-0.176212	3.641182	1.904728
96	C	-1.453024	3.289851	2.338107
97	H	-1.946848	2.427230	1.905451
98	C	-2.109419	4.073004	3.286455
99	H	-3.106455	3.796221	3.617914
100	C	-1.497748	5.210666	3.801220
101	H	-2.009509	5.819670	4.540287
102	C	-0.229926	5.576618	3.353175
103	H	0.246920	6.473323	3.737124
104	C	0.426721	4.800964	2.404257
105	H	1.408965	5.103015	2.052852
106	C	0.515267	3.894170	-0.864317
107	C	1.515357	4.794361	-1.230670
108	H	2.479421	4.782119	-0.733373
109	C	1.272646	5.733317	-2.231912

110	H	2.055647	6.431722	-2.511719
111	C	0.031488	5.788859	-2.857693
112	H	-0.155435	6.527385	-3.631374
113	C	-0.976051	4.906015	-2.475102
114	H	-1.954210	4.961405	-2.944502
115	C	-0.736510	3.961070	-1.482722
116	H	-1.527596	3.285210	-1.165995
117	C	-1.921832	0.859741	0.026063
118	C	-3.139652	1.113037	0.040173
119	C	-4.495111	1.440970	0.085421
120	C	-5.367112	1.706822	-1.029086
121	H	-5.058205	1.708215	-2.065580
122	C	-6.665433	2.021827	-0.541175
123	H	-7.518519	2.307091	-1.143035
124	C	-6.650044	1.864120	0.875339
125	H	-7.488680	2.009374	1.543814
126	C	-5.341601	1.450904	1.251898
127	H	-5.007544	1.229690	2.256684
128	C	-6.736791	-1.482461	-1.412336
129	H	-6.632461	-1.399776	-2.485896
130	C	-7.879741	-1.111944	-0.651856
131	H	-8.804272	-0.711399	-1.046931
132	C	-7.574465	-1.319404	0.724446
133	H	-8.235618	-1.127846	1.559277
134	C	-6.241208	-1.827888	0.803027
135	H	-5.706313	-2.089171	1.706010
136	C	-5.733471	-1.935438	-0.519311
137	H	-4.732717	-2.241862	-0.796498

Table S4. Partial molecular orbital contribution (%) of complex $[\mathbf{1}]^+$ in dichloromethane media calculated by TDDFT method at the PBE1PBE level.

orbital	energy (eV)	MO contribution (%)					
		Ru (s/p/d)	tppz	C≡C	PPh_3	Fe (s/p/d)	Cp
LUMO+4	-1.20	0.69 (6/50/44)	88.99	0.07	9.98	0.15 (4/79/17)	0.12
LUMO+1	-2.48	8.87 (0/24/76)	83.01	0.62	6.94	0.25 (4/8/88)	0.31
LUMO	-2.71	1.90 (1/6/93)	96.00	0.12	1.92	0.00 (26/72/2)	0.06
HOMO	-5.36	19.74 (0/0/100)	4.61	25.56	7.93	25.23 (1/4/96)	16.93
HOMO-4	-6.31	67.54 (0/0/100)	21.31	0.04	11.10	0.00 (25/26/49)	0.00
HOMO-7	-6.94	5.95 (0/1/99)	80.02	0.08	13.84	0.01 (32/49/20)	0.09

Table S5. Absorption transition character for complex $[\mathbf{1}]^+$ in dichloromethane media calculated by TDDFT method at the PBE1PBE level along with the experimental data.

	E, nm (eV)	O.S.	contribution	assignment	exp. (nm)
S_4	561 (2.21)	0.0945	HOMO→LUMO+1 (74%)	MLCT/LLCT	521
S_{10}	452 (2.74)	0.0861	HOMO-4→LUMO (87%)	MLCT/IL	482
S_{25}	351 (3.54)	0.177	HOMO-7→LUMO (53%)	IL/LLCT	330
			HOMO→LUMO+4 (20%)	LLCT/ MLCT	

Table S6. Partial molecular orbital contribution (%) of complex [**1a**]$^{2+}$ in dichloromethane media calculated by TDDFT method at the PBE1PBE level.

orbital	energy (eV)	MO contribution (%)					
		Ru (s/p/d)	tppz	C≡C	PPh_3	Fe (s/p/d)	Cp[a]
*α*LUMO+1	-3.06	1.97 (1/9/89)	95.86	0.14	1.94	0.01 (3/31/67)	0.08
*α*LUMO	-3.19	1.84 (5/78/16)	17.23	5.10	4.99	35.14 (0/1/99)	35.69
*α*HOMO	-6.31	60.72 (0/1/99)	11.89	17.89	3.58	0.39 (2/16/82)	5.54
*α*HOMO-1	-6.43	38.08 (0/0/99)	5.81	21.58	10.22	8.44 (3/21/76)	15.87
*α*HOMO-2	-6.80	64.55 (0/0/100)	25.39	0.17	9.84	0.00 (1/22/77)	0.04
*α*HOMO-4	-7.27	11.12 (0/1/99)	76.49	0.07	12.25	0.01 (46/45/9)	0.06
*β*LUMO+2	-2.85	7.38 (0/26/74)	80.11	0.72	5.61	4.50 (0/1/99)	1.67
*β*LUMO+1	-3.34	1.97 (1/9/90)	95.89	0.13	1.94	0.01 (6/63/31)	0.07
*β*LUMO	-6.41	1.39 (3/48/49)	8.01	4.90	3.20	53.18 (0/0/100)	29.32
*β*HOMO	-6.80	60.58 (0/1/99)	11.84	17.86	3.61	0.45 (2/11/87)	5.65
*β*HOMO-1	-8.45	38.54 (0/1/99)	5.93	22.04	10.44	6.72 (3/17/81)	16.33
*β*HOMO-2	-3.34	64.55 (0/0/100)	25.40	0.17	9.83	0.00 (1/16/84)	0.04
*β*HOMO-4	-6.41	11.12 (0/1/99)	76.47	0.08	12.26	0.01 (44/41/15)	0.06
*β*HOMO-21	-6.80	0.62 (0/12/88)	0.83	1.39	0.92	90.26 (2/0/98)	5.99

Table S7. Absorption transition character for complex [**1a**]$^{2+}$ in dichloromethane media calculated by TDDFT method at the PBE1PBE level, along with the experimental data.

States	*E*, nm (eV)	O.S.	contribution	assignment	exp. (nm)
S_2	1358 (0.91)	0.0018	*β*HOMO-21→*β*LUMO (91%)	MLCT	1247
			*β*HOMO-21→*β*LUMO+2 (7%)	MLCT/IVCT	
S_8	571 (2.17)	0.1690	*α*HOMO-1→*α*LUMO (40%)	MLCT/LLCT	526
			*β*HOMO-1→*β*LUMO (16%)	IVCT/LLCT	
S_{27}	426 (2.91)	0.1833	*α*HOMO-2→*α*LUMO +1 (34%)	MLCT/ILCT	471
			*β*HOMO-2→*β*LUMO+1 (30%)	MLCT/ILCT	
S_{51}	352 (3.52)	0.2024	*β*HOMO-4→*β*LUMO+1 (37%)	ILCT/MLCT/LLCT	360
			*α*HOMO-4→*α*LUMO +1 (36%)	ILCT/MLCT/LLCT	

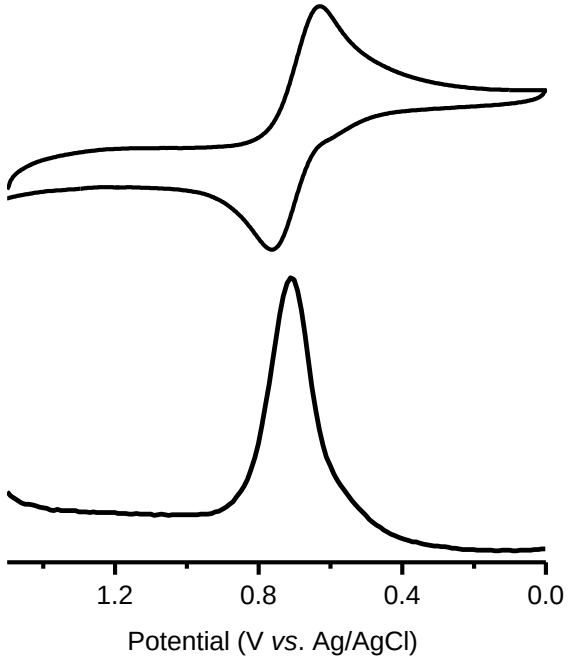


Fig. S1. Plots of Cyclic (top) and differential pulse (lower) voltammograms of FcC≡CH in 0.1 M dichloromethane-$TBAPF_6$ solution. The scan rate is 100 mV s^{-1} for CV and 20 mV s^{-1} for DPV.

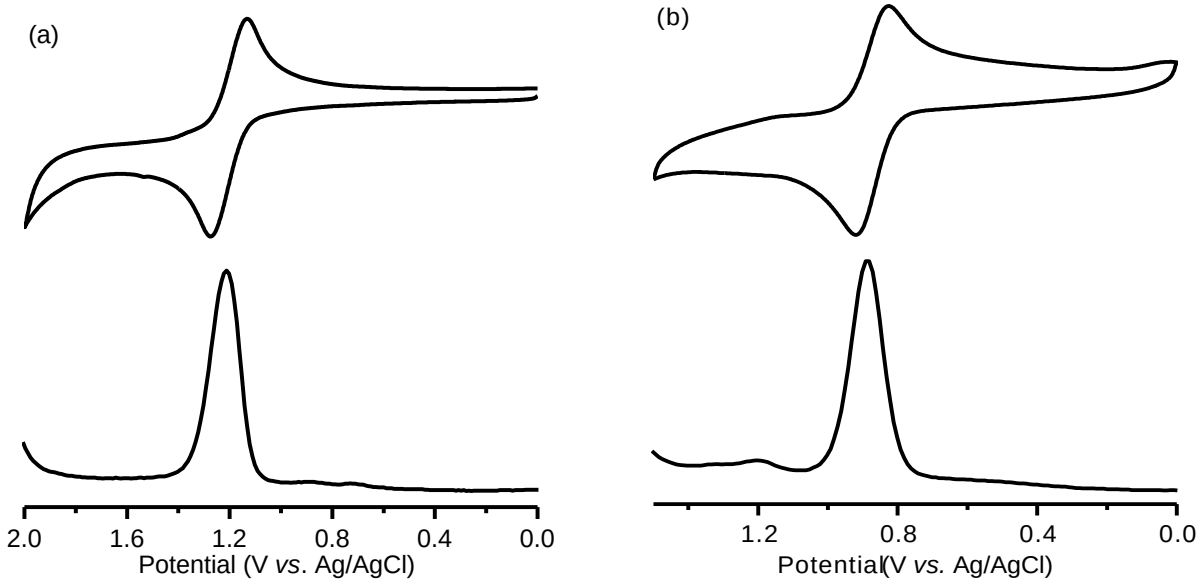


Fig. S2. Plots of cyclic (top) and differential pulse (bottom) voltammograms of (a) $[(tppz)(PPh_3)_2RuCl](ClO_4)$ and (b) [**4**](ClO_4) in 0.1 M dichloromethane-$TBAPF_6$ solution. The scan rate is 100 mV s^{-1} for CV and 20 mV s^{-1} for DPV.

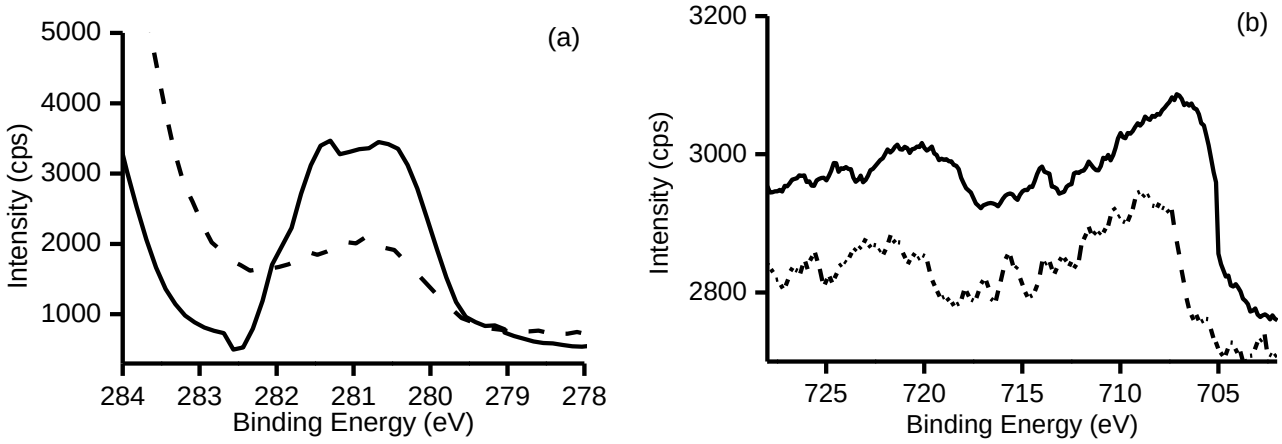


Fig. S3. The binding energy of (a) Ru $3d_{5/2}$ and (b) Fe $2P_{1/2}$ and Fe $2P_{3/2}$ of $[\mathbf{1}]^{+}$ (solid) and $[\mathbf{1a}]^{2+}$ (dash).

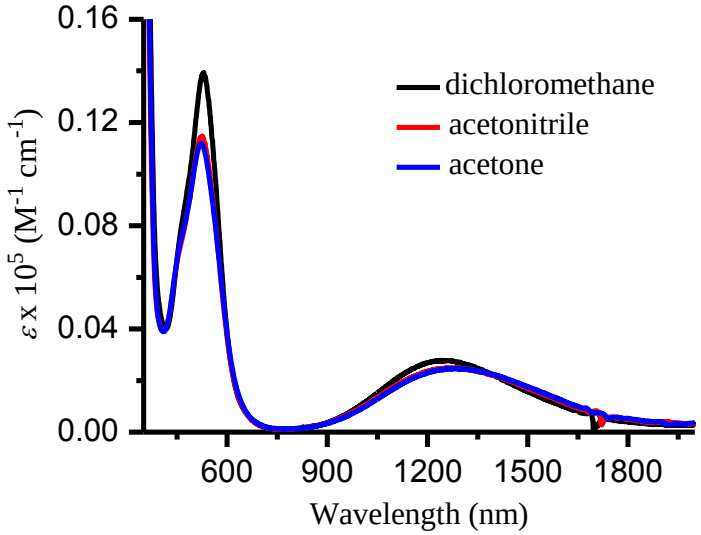


Fig. S4. Visible and near−IR electronic absorption spectra of mixed-valence complex $[\mathbf{1a}]^{2+}$ in different solvents.

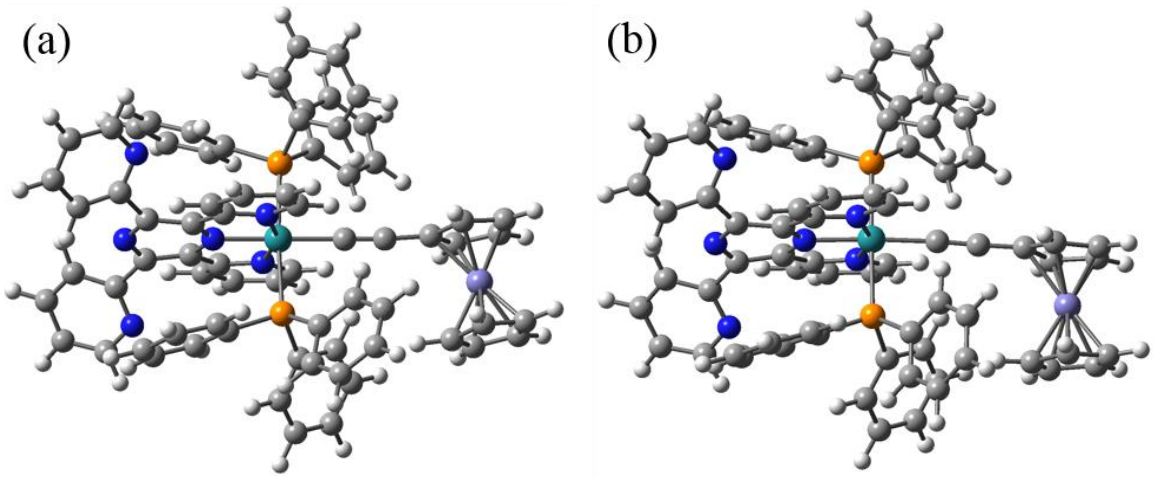
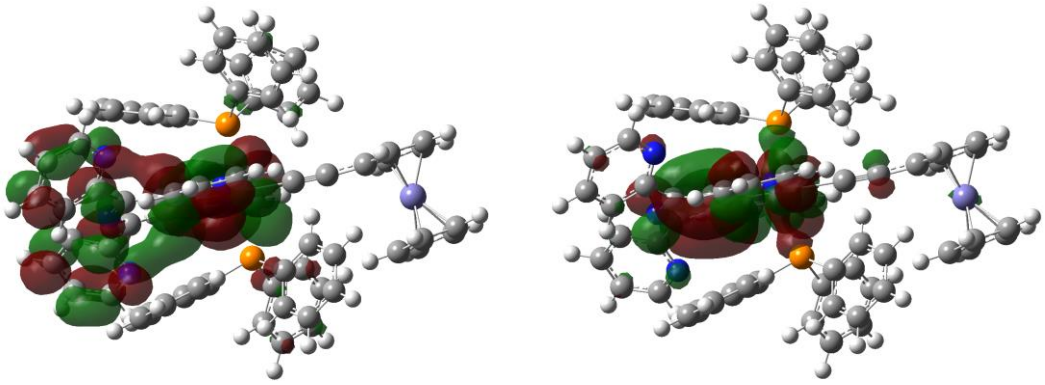


Fig. S5. Optimized structures of complexes $[\mathbf{1}]^{+}$ (a) and $[\mathbf{1a}]^{2+}$ (b) in the ground state by DFT method at PBE1PBE level. Green, purple, yellow, blue, gray, and white spheres represent the ruthenium, iron, phosphorus, nitrogen, carbon, and hydrogen atoms, respectively.



LUMO+4 LUMO+1

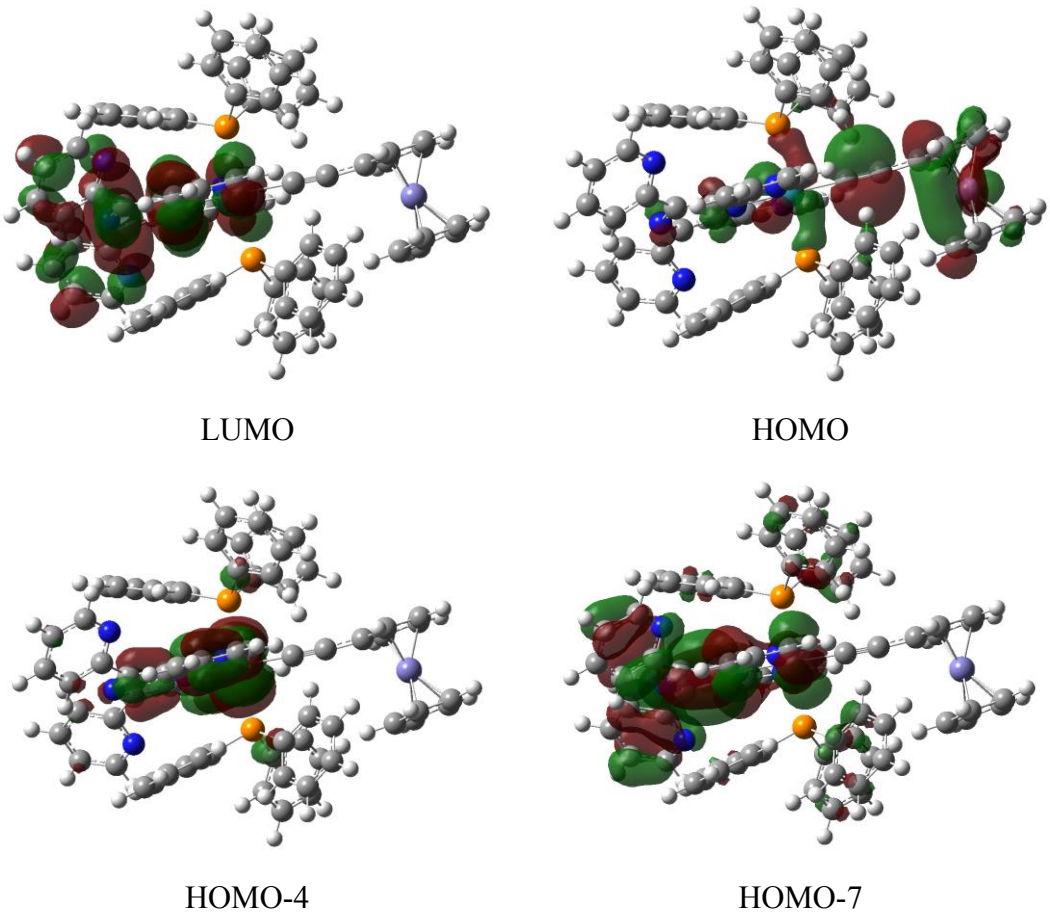
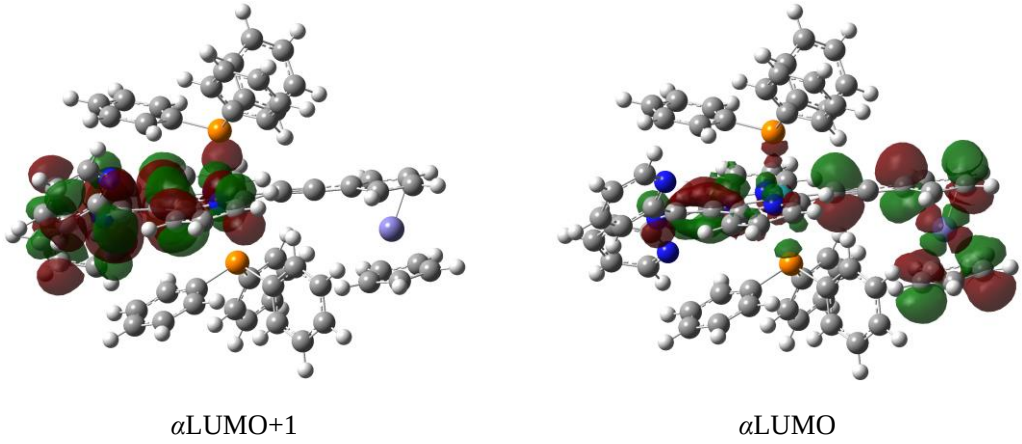
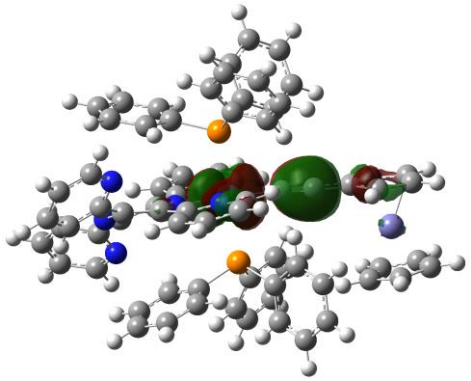
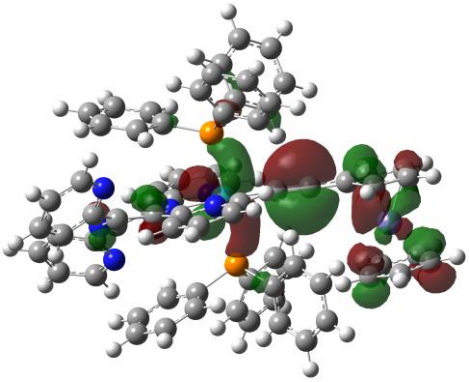


Fig. S6. Plots of the molecular orbitals involved in the absorption transitions for complex $[\mathbf{1}]^{+}$ in dichloromethane media by TDDFT method at the PBE1PBE level.

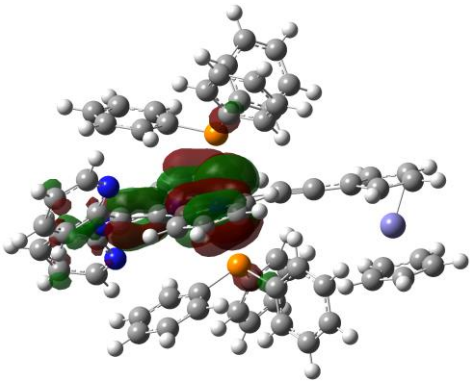




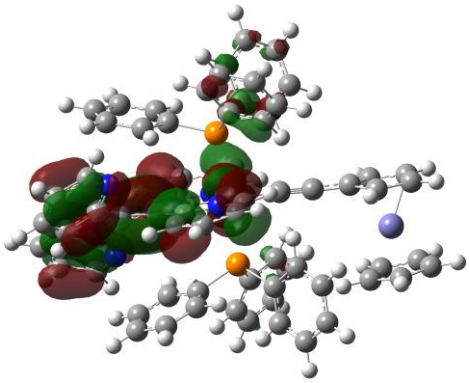
*α*HOMO



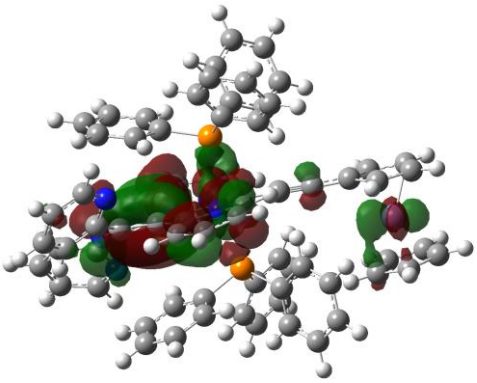
*α*HOMO-1



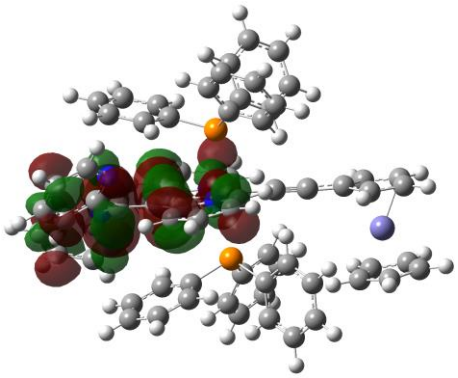
*α*HOMO-2



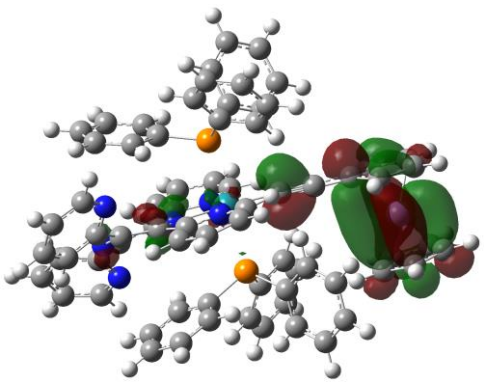
*α*HOMO-4



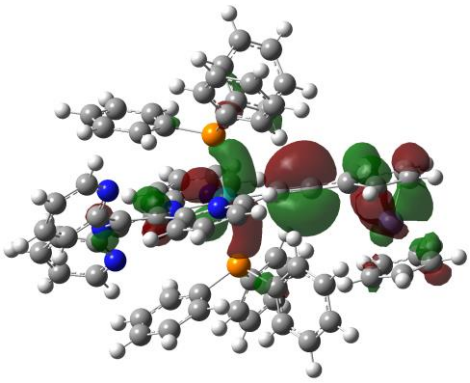
*β*LUMO+2



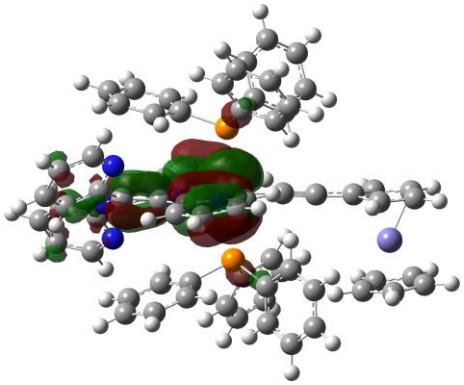
*β*LUMO+1



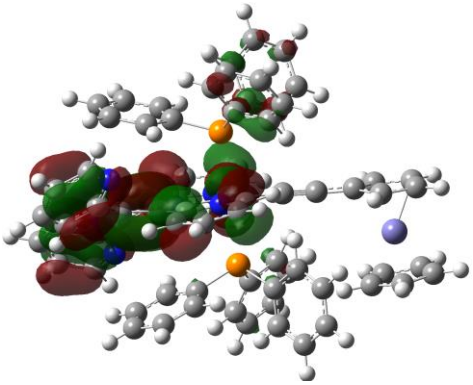
*β*LUMO



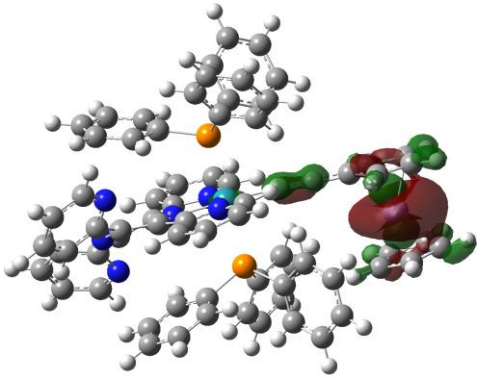
*β*HOMO-1



*β*HOMO-2



*β*HOMO-4



*β*HOMO-21

Fig. S7. Plots of the molecular orbital involved in the absorption transitions for complex [**1a**]$^{2+}$ in dichloromethane media.