Supporting information
The impact of substituent nature in diphormylpyridile Schiff base on photophysical and electrochemical properties of ruthenium and iron-based complexes

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Content

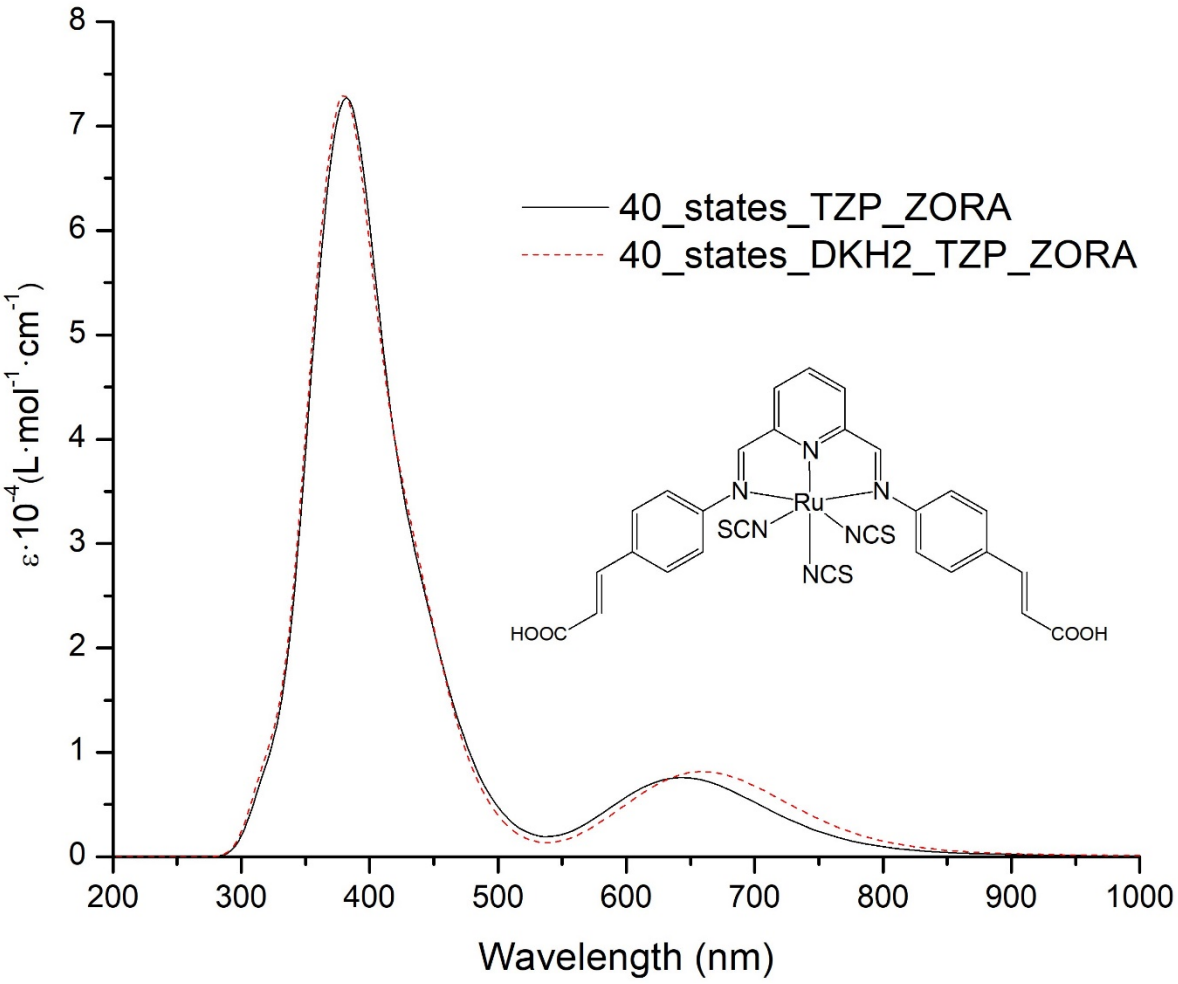


Figure S1 Modeling electron absorption spectra for Ru(II)-based complex at TD-B3LYP/6-311G(d,p) for non-metal atoms and TZP-ZORA* for Ru atoms level of theory with using second-order Douglas-Kroll-Hess method.

* TZP-ZORA, all-electron triple-zeta basis for calculations with the ZORA approach A. Canal Neto, I. B. Ferreira, F. E. Jorge, A. Z. de Oliveira, Chem. Phys. Lett. 771, 138548 (2021) 10.1016/j.cplett.2021.138548

Table S1 The calculated metal-ligand bond lengths, Å, for the optimized complexes (B3LYP/6-311G(d,p), Lanl2DZ)

Substituent-R	M-N_{py}	M-N_{hyd}	M-NCS_{axial}	M-$NCS_{equatorial}$	M-N_{py}	M-N_{hyd}	M-NCS_{axial}	M-$NCS_{equatorial}$
	Fe(II)				Fe(III)			
H	1.89	2.06	1.97	1.95	1.90	2.05	1.89	1.93
CH_3	1.89	2.06	1.97	1.96	1.91	2.08	1.91	1.89
COOH	1.88	2.06	1.97	1.95	1.91	2.08	1.91	1.88
NH_2	1.90	2.07	1.97	1.96	1.91	2.08	1.91	1.89
NO_2	1.87	2.06	1.96	1.94	1.91	2.08	1.91	1.89
OH	1.90	2.06	1.96	1.97	1.91	2.08	1.91	1.89
	Ru(II)				Ru(III)			
H	1.96	2.13	2.06	2.08	2.01	2.16	2.02	2.03
CH_3	1.96	2.13	2.06	2.08	2.01	2.16	2.02	2.03
COOH	1.95	2.13	2.05	2.08	1.99	2.20 (2.12)	2.02	2.03
NH_2	1.97	2.13	2.06	2.08	2.01	2.16	2.03	2.03
NO_2	1.94	2.13	2.05	2.07	1.99	2.21 (2.11)	2.02	2.03
OH	1.97	2.13	2.06	2.08	2.01	2.16	2.02	2.03

Table S2 Selected harmonic vibrational frequencies (cm^{-1}) for diphormylpyridile Schiff bases and ruthenium and iron complexes predicted by the B3LYP functional.

Type of vibration	Ligand	Ru(II) complexes	Ru(III) complexes	Fe(II) complexes	Fe(III) complexes
	ν, cm^{-1}/Intensity	ν, cm^{-1}/ Intensity	ν, cm^{-1} /Intensity	ν, cm^{-1}/ Intensity	ν, cm^{-1}/ Intensity
R=H					
$C=N_{py}$	1468/0.09	1375/145.8	1439/53.3	1438/59	1457/82
		1407/63.7			
$C=N_{azom}$				1654/66	1656/18
$R=CH_3$					
$C=N_{azom}$	1699/32.7	1554/24.1	1577/41.9	1552/18	1575/170
$C=N_{py}$	1477/0.17	1442/36	1469/28.3	1458/82	1475/18
$C=N_{azom}$	1700/39	1582/28.3	1600/20.8	1621/106	1608/1
	1700.3/40				
R=COOH					
$C=N_{py}$	1469/10.3	1387/625	1403/235.3	1398/394	1410/126
		1441/31.1	1458/6.5		
$C=N_{azom}$	1698/21.8	1581/59.3	1590/49.8	1607/12	1571/260
	1699/18.4				1661/4
$R=NH_2$					
$C=N_{py}$	1485/10.6	1408/0.4	1416/9.8	1476/192	1502/139
$C=N_{azom}$	1702/65.8	1585/57.7	1587/2.3	1559/9	1576/194
	1703/46.3			1608/27	1612/4
$R=NO_2$					
$C=N_{py}$	1460/0.1	1378/17.8	1438/8.9	1429/20	1447/28
		1418/23.5			
$C=N_{azom}$	1695/7.3	1576/77	1584/129.4	1605/253	1567/501
R=OH					
$C=N_{py}$	1483/10.9	1398/9.5	1408/82.8	1464/230	1482/153
			1479/274		
$C=N_{azom}$	1701/33	1581/20.6	1592/14	1560/23	1579/261
	1702/52.8		1600/76.1	1607/18	1609/2

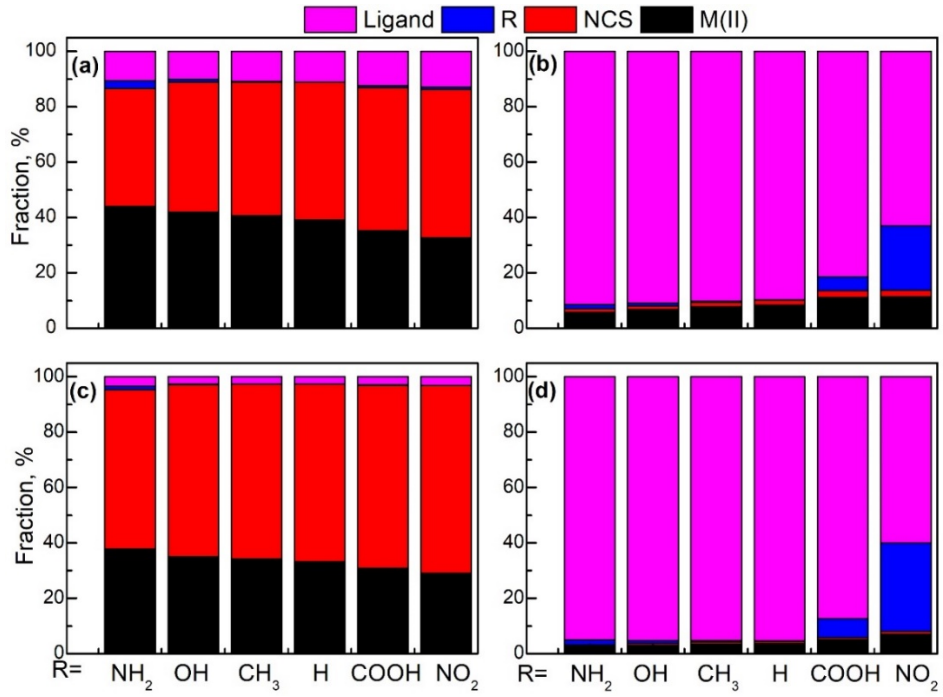


Figure S2. Molecular orbital composition (%) of the HOMO (a for Ru(II) and c for Fe(II) complexes) and LUMO (b for Ru(II) and d for Fe(II) complexes). MO of the calculated complexes is divided on four components: organic ligand, substituent R, NCS ligands and metal center.

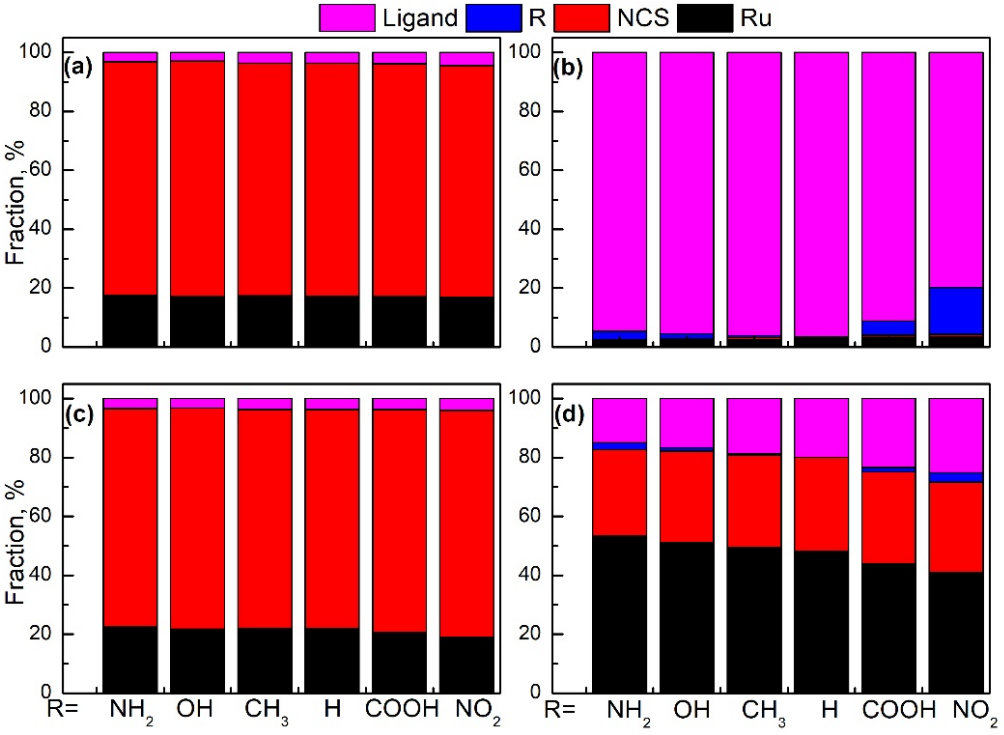


Figure S3. Molecular orbital composition (%) of the HOMO (a for alpha and c for beta MO of Ru(III) complexes) and LUMO (b for alpha and d for beta MO of Ru(III) complexes). MO of the calculated complexes is divided on four components: organic ligand, substituent R, NCS ligands and metal center.

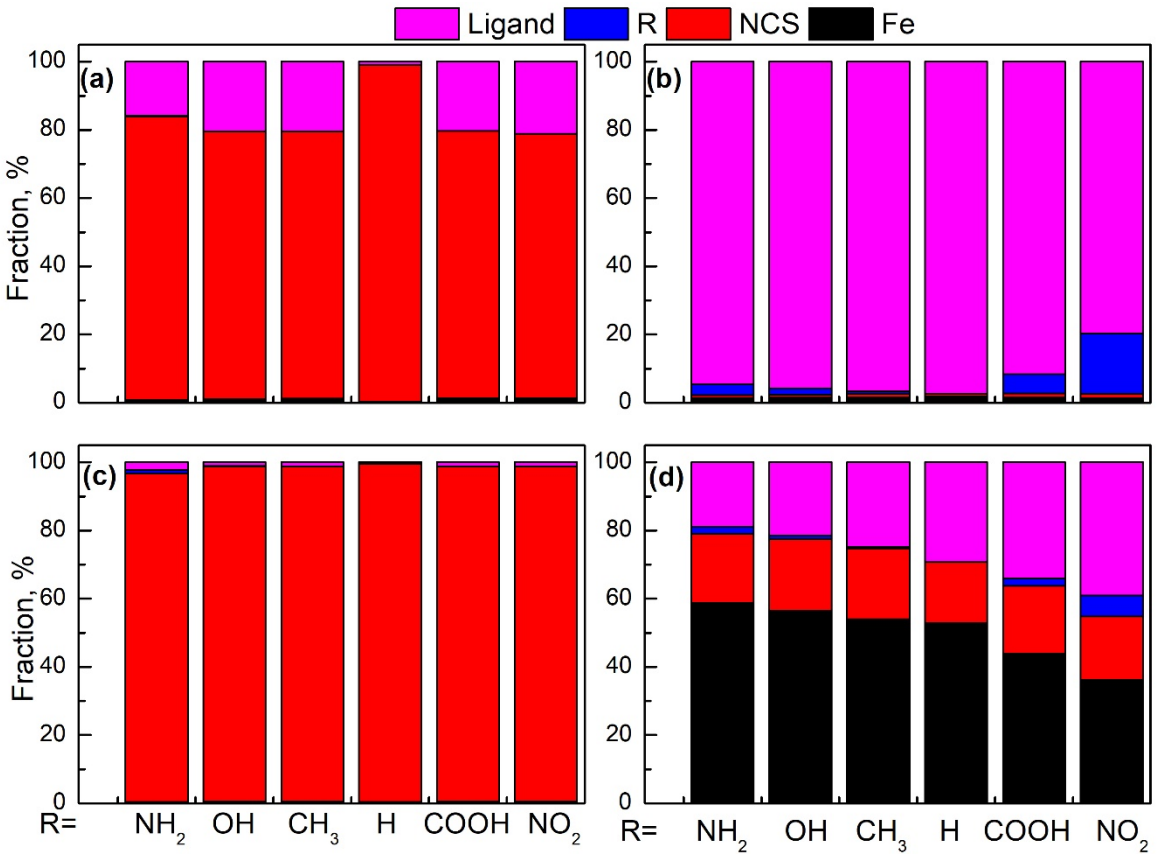


Figure S4. Molecular orbital composition (%) of the HOMO (a for alpha and c for beta MO of Fe(III) complexes) and LUMO (b for alpha and d for beta MO of Fe(III) complexes). MO of the calculated complexes is divided on four components: organic ligand, substituent R, NCS ligands and metal center.

Table. S3. Calculated by TD-DFT electronic transitions and their assignment for ligand system. Selected calculated optical transitions with oscillator strengths (f > 0.1), wavelengths (λ, nm) and main orbital transition contributions (>10%) H – HOMO, L – LUMO. The selected calculated electron transitions, Λ parameters values and Δr-index for ligand system by using cam-b3lyp/6-311G(d,p) level of theory.

No.	λ (nm)	f	Major contribs	Λ	Δr-index, Å
R=NH_2					
1	338	1.4399	H-1->L+1 (32%), HOMO->LUMO (52%)	0.69743	0.54
4	278	0.8608	H-7->L+1 (12%), H-1->L+2 (14%), HOMO->L+3 (15%)	0.591482	1.16
2	327	0.4654	H-1->LUMO (39%), HOMO->L+1 (40%)	0.726876	0.6
19	215	0.3388	H-5->LUMO (16%), H-4->L+1 (13%), H-1->L+4 (30%), HOMO->L+5 (33%)	0.564827	0.61
33	189	0.3111	H-5->LUMO (11%), H-5->L+5 (15%), H-4->L+1 (12%), H-4->L+4 (15%)	0.675798	0.67
5	276	0.2465	H-7->LUMO (16%), H-1->L+3 (21%), HOMO->L+1 (12%), HOMO->L+2 (14%)	0.654094	0.83
24	202	0.1935	H-7->L+2 (10%), H-5->L+3 (20%), H-4->L+2 (24%)	0.522054	1.04
34	189	0.1875	H-8->L+1 (11%), H-5->L+1 (10%), H-5->L+4 (14%), H-4->L+5 (14%)	0.689088	0.59
26	201	0.1467	H-2->L+1 (18%), H-2->L+2 (47%)	0.469397	3.13
37	180	0.1419	H-16->LUMO (19%), H-15->L+1 (18%)	0.585724	0.83
32	191	0.1252	H-5->LUMO (26%), H-4->L+1 (35%)	0.544441	0.9
12	247	0.1251	H-3->L+1 (15%), H-1->LUMO (26%), HOMO->L+1 (24%), HOMO->L+2 (19%)	0.708576	0.89
16	235	0.1217	H-1->LUMO (17%), H-1->L+3 (21%), HOMO->L+2 (11%)	0.670865	0.9
23	203	0.108	H-2->LUMO (13%), H-2->L+3 (34%)	0.525865	2.53
18	219	0.1077	H-7->LUMO (15%), H-3->L+1 (43%)	0.654422	1.29
R=OH					
1	342	1.3743	H-1->L+1 (30%), HOMO->LUMO (50%)	0.674171	2.24
3	280	0.8023	H-7->L+1 (13%), H-5->LUMO (10%)	0.567632	3.26
2	329	0.4339	H-1->LUMO (38%), HOMO->L+1 (39%)	0.698177	1.86
31	190	0.3121	H-8->LUMO (11%), H-4->L+4 (12%)	0.610518	2.99
19	215	0.2886	H-1->L+4 (27%), HOMO->L+4 (13%), HOMO->L+5 (19%)	0.520938	3.86
4	277	0.2799	H-7->LUMO (16%), H-1->L+2 (12%), HOMO->L+1 (12%)	0.581688	2.98
24	203	0.2633	H-3->L+3 (40%), H-2->L+3 (12%)	0.508547	2.81
36	180	0.2148	H-16->L+1 (12%)	0.576113	2.49
18	218	0.1775	H-7->LUMO (10%), H-5->L+1 (38%)	0.62843	2.36

32	190	0.1711	H-8->L+1 (13%), H-3->L+5 (15%)	0.61987	2.61
20	215	0.1545	H-2->LUMO (11%), H-1->L+5 (24%), HOMO->L+4 (17%), HOMO->L+5 (15%)	0.532392	3.63
R=CH_3					
1	344	1.4142	H-1->L+1 (29%), HOMO->LUMO (56%)	0.69152	0.77
3	284	0.5301	H-5->LUMO (34%), H-5->L+2 (12%), H-2->LUMO (15%)	0.586043	1.28
2	330	0.4438	H-1->LUMO (42%), HOMO->L+1 (38%)	0.720545	0.87
24	203	0.3013	H-4->L+2 (34%), H-3->L+3 (29%)	0.497135	0.99
5	278	0.2916	H-6->LUMO (11%), H-1->L+2 (21%), HOMO->L+1 (15%), HOMO->L+3 (11%)	0.668137	0.95
20	212	0.2648	H-7->LUMO (16%), H-6->LUMO (33%), H-6->L+2 (10%), H-2->L+1 (18%)	0.654735	1.35
19	215	0.218	H-4->LUMO (16%), H-1->L+5 (25%), HOMO->L+4 (22%), HOMO->L+5 (10%)	0.570282	1.13
6	270	0.1932	H-2->LUMO (10%), H-1->L+1 (22%), HOMO->L+2 (30%)	0.647044	0.9
31	190	0.1765	H-8->LUMO (15%)	0.650694	0.94
27	196	0.1703	H-11->L+1 (16%), H-8->LUMO (10%), H-4->LUMO (11%), H-3->L+1 (11%), H-2->L+2 (11%)	0.636085	0.86
4	278	0.1583	H-8->LUMO (16%), H-5->LUMO (20%), H-5->L+2 (11%)	0.608709	1.03
30	193	0.156	H-4->LUMO (17%), H-3->L+1 (30%), H-3->L+3 (12%), H-2->L+2 (10%)	0.563413	1.05
32	190	0.1371	H-8->L+1 (14%), H-4->L+5 (10%), H-3->L+4 (11%)	0.681295	0.95
39	179	0.1097	H-4->L+5 (12%), H-3->L+4 (14%), H-2->L+3 (12%), H-1->L+6 (11%)	0.70223	1.27
R=H					
1	346	1.3809	H-1->L+1 (28%), HOMO->LUMO (57%)	0.685938	0.8
2	331	0.4177	H-1->LUMO (42%), HOMO->L+1 (37%)	0.705975	0.8
30	192	0.3521	H-11->L+1 (13%), H-3->L+1 (16%), H-2->L+2 (11%)	0.628225	0.79
3	287	0.3509	H-5->LUMO (48%), H-5->L+2 (17%)	0.576226	0.99
4	280	0.3456	H-7->LUMO (20%), H-6->L+1 (12%), H-2->LUMO (13%)	0.620126	0.55
5	279	0.3058	H-6->LUMO (19%), H-1->L+2 (22%), HOMO->L+1 (17%), HOMO->L+3 (11%)	0.66086	0.52
23	204	0.3054	H-4->L+2 (20%), H-3->L+3 (28%), H-2->L+2 (21%)	0.545428	0.72
17	216	0.2217	H-10->L+1 (10%), H-2->LUMO (16%), H-1->L+5 (18%), HOMO->L+4 (21%)	0.625922	0.5
6	271	0.2015	H-4->LUMO (12%), H-1->L+1 (25%), HOMO->L+2 (32%)	0.668871	0.61
31	191	0.169	H-7->LUMO (14%), H-6->L+1 (14%)	0.635843	0.52
27	196	0.1611	H-11->L+1 (10%), H-4->LUMO (13%), H-3->L+1 (27%)	0.593818	0.71
32	190	0.1436	H-7->L+1 (15%), H-3->L+4 (10%)	0.678929	0.61

37	180	0.1087	H-16->L+1 (24%), H-15->LUMO (26%)	0.581159	0.87
19	214	0.1046	H-10->L+1 (24%), H-4->LUMO (20%), H-1->L+5 (11%), HOMO->L+4 (10%)	0.649095	0.7
R=COOH					
1	354	1.2295	H-1->L+1 (23%), HOMO->LUMO (59%)	0.62171	1.92
6	279	0.7982	H-7->LUMO (15%), H-1->L+1 (15%), H-1->L+3 (12%), HOMO->L+2 (30%)	0.626817	0.95
34	193	0.5116	H-12->L+1 (19%), H-10->L+3 (10%), H-4->L+2 (15%)	0.670373	1.95
2	337	0.4063	H-1->LUMO (42%), HOMO->L+1 (33%)	0.626655	1.84
5	282	0.3801	H-5->LUMO (18%), H-1->L+2 (22%), HOMO->L+1 (25%)	0.640481	1.31
37	187	0.2707	H-11->L+1 (13%), H-3->L+5 (17%), H-2->L+6 (11%)	0.611323	2.54
23	209	0.1973	H-10->L+1 (16%), H-6->LUMO (16%)	0.599246	1.32
3	298	0.1959	H-7->LUMO (39%), H-6->LUMO (30%), H-4->LUMO (10%)	0.585945	0.92
24	208	0.182	H-10->L+1 (11%), H-3->L+2 (17%), H-2->L+1 (13%)	0.492541	2.2
25	207	0.1815	H-3->L+1 (13%), H-2->L+2 (18%), H-1->L+6 (10%), HOMO->L+5 (11%)	0.509591	2.12
28	200	0.1681	H-6->L+2 (10%), H-3->LUMO (10%), H-2->L+1 (16%), H-2->L+3 (13%)	0.493695	2.28
22	211	0.1492	H-10->LUMO (12%), H-1->L+2 (24%), HOMO->L+3 (17%)	0.634589	1.43
26	204	0.1307	H-12->LUMO (26%), H-6->L+1 (17%), H-5->L+2 (15%)	0.631788	0.73
38	186	0.1079	H-3->L+6 (11%), H-2->L+5 (16%)	0.67868	1.7
R=NO_2					
1	364	1.0423	H-1->L+1 (19%), HOMO->LUMO (53%), HOMO->L+2 (11%)	0.507759	3.26
7	284	0.863	H-9->LUMO (14%), H-5->L+1 (10%), H-1->L+3 (10%), HOMO->L+2 (14%)	0.551291	1.86
40	191	0.4319	H-4->L+4 (12%), H-3->L+6 (14%), H-2->L+5 (15%)	0.664872	0.93
25	212	0.4029	H-12->LUMO (10%), H-4->L+1 (14%), H-3->L+1 (16%), H-1->L+6 (10%), HOMO->L+5 (11%)	0.567427	1.54
2	343	0.3701	H-1->LUMO (34%), H-1->L+2 (13%), HOMO->L+1 (30%)	0.540672	2.76
38	193	0.3253	H-16->LUMO (44%)	0.601444	1.92
6	289	0.3082	H-1->LUMO (32%), H-1->L+2 (12%), HOMO->L+1 (37%)	0.565301	2.74
30	203	0.2411	H-3->L+4 (14%), H-2->L+1 (10%), H-2->L+3 (30%)	0.458107	1.17
5	301	0.2101	H-9->LUMO (60%), H-6->LUMO (12%)	0.480831	2.18
39	191	0.1808	H-4->L+3 (10%), H-3->L+5 (12%), H-2->L+6 (11%)	0.653486	1.62
26	212	0.1806	H-2->L+1 (27%), H-1->L+5 (18%), HOMO->L+6 (20%)	0.492273	1.42
23	223	0.1473	H-12->LUMO (21%), H-10->LUMO (32%)	0.56439	2.72

8	277	0.1299	H-6->L+1 (15%), H-5->LUMO (10%), H-1->LUMO (27%), HOMO->L+3 (10%)	0.50291	2.53
24	216	0.1163	H-6->LUMO (42%)	0.486394	2.6

Table. S4. Calculated by TD-DFT electronic transitions and their assignment for Ru(II) and Fe(II) complex. Selected calculated optical transitions with oscillator strengths (f > 0.01), wavelengths (λ, nm) and main orbital transition contributions (>10%) H – HOMO, L – LUMO. The selected calculated electron transitions, Λ parameters values and Δr-index for Ru(II) and Fe(II) complexes by using cam-b3lyp/6-311G(d,p),Lanl2dz level of theory

No.	λ (nm)	f	Major contribs	Λ	Δr-index, Å	No.	λ (nm)	f	Major contribs	Λ	Δr-index, Å
Ru(II)-complex						Fe(II)-complex					
R=NH_2											
10	340	0.9769	H-7->L+1 (13%), H-6->LUMO (65%)	0.56526	1.44	13	332	0.9194	H-7->L+1 (16%), H-6->LUMO (56%)	0.555173	1.57
11	326	0.4874	H-7->LUMO (14%), H-6->L+1 (24%), H-4->LUMO (44%)	0.450224	1.45	14	322	0.5006	H-7->LUMO (14%), H-6->L+1 (26%), H-4->LUMO (39%)	0.446375	1.25
15	312	0.2907	H-7->LUMO (37%), H-6->L+1 (15%), H-4->LUMO (38%)	0.469494	1.48	18	305	0.3753	H-7->LUMO (30%), H-6->L+1 (19%), H-4->LUMO (38%)	0.474324	1.22
36	253	0.229	H-7->L+3 (25%), H-6->L+2 (25%), H-2->L+3 (13%)	0.488423	0.94	21	292	0.1566	H-9->LUMO (15%), H-7->L+1 (22%), H-3->L+1 (32%)	0.337392	1.72
19	294	0.1337	H-7->L+1 (20%), H-4->L+1 (44%)	0.346086	1.61	30	260	0.1155	H-9->LUMO (10%), H-7->L+3 (11%), H-6->L+2 (19%), HOMO->L+3 (19%)	0.441389	1.13
						15	313	0.1108	H-4->LUMO (10%), H-3->LUMO (73%)	0.189888	2.01
						26	271	0.1074	H-10->L+1 (26%), H-2->L+1 (17%), H-2->L+3 (12%)	0.317528	2.03
R=OH											
9	345	0.9224	H-7->L+1 (13%), H-6->LUMO (62%)	0.552694	1.76	13	337	0.8677	H-7->L+1 (15%), H-6->LUMO (53%)	0.530738	2.29
14	318	0.4038	H-7->LUMO (44%), H-6->L+1 (20%), H-4->LUMO (23%)	0.492163	1.93	17	312	0.4809	H-7->LUMO (35%), H-6->L+1 (23%), H-4->LUMO (23%)	0.481506	2.11
11	331	0.3325	H-6->L+1 (18%), H-4->LUMO (51%), H-3->LUMO (12%)	0.394615	1.71	14	328	0.3626	H-6->L+1 (19%), H-4->LUMO (46%), H-3->LUMO (10%)	0.372104	1.84
36	254	0.2581	H-7->L+3 (26%), H-6->L+2 (21%)	0.516266	2.26	21	296	0.2416	H-9->LUMO (37%), H-7->L+1 (25%), H-1->LUMO (11%)	0.423022	1.94

19	299	0.1667	H-9->LUMO (18%), H-7->L+1 (24%), H-4->L+1 (30%)	0.359431	1.74	29	262	0.1543	H-9->LUMO (10%), H-7->L+3 (12%), H-6->L+2 (19%)	0.48443	2.53
25	280	0.1123	H-10->L+1 (14%), H-8->L+1 (11%), H-2->L+1 (10%), H-2->L+3 (18%)	0.352051	2.21	31	256	0.1158	H-7->L+3 (12%), HOMO->L+2 (20%)	0.410964	2.77
16	308	0.1024	H-9->LUMO (14%), H-4->L+1 (16%), H-3->L+1 (44%)	0.249643	2.44	26	274	0.1034	H-10->L+1 (27%), H-2->L+1 (17%)	0.29955	2.61
R=CH_3											
9	347	0.9042	H-7->L+1 (11%), H-6->LUMO (69%)	0.564494	1.54	13	340	0.7896	H-7->L+1 (11%), H-6->LUMO (60%)	0.536489	1.84
14	319	0.4926	H-7->LUMO (52%), H-6->L+1 (21%), H-4->LUMO (13%)	0.516767	1.94	17	313	0.5933	H-7->LUMO (43%), H-6->L+1 (27%), H-4->LUMO (13%)	0.525565	1.96
16	305	0.2727	H-9->LUMO (36%), H-7->L+1 (10%), H-4->L+1 (19%)	0.402052	1.46	14	330	0.2634	H-6->L+1 (13%), H-4->LUMO (58%), H-3->LUMO (12%)	0.339499	1.28
11	333	0.2533	H-6->L+1 (13%), H-4->LUMO (58%), H-3->LUMO (15%)	0.368251	1.64	21	296	0.25	H-8->LUMO (26%), H-7->L+1 (26%), H-4->L+1 (26%)	0.398138	1.24
36	253	0.2244	H-7->L+3 (24%), H-6->L+2 (22%), H-2->L+3 (11%)	0.497187	1	29	263	0.1545	H-7->L+3 (13%), H-6->L+2 (20%), HOMO->L+3 (11%)	0.448558	1.05
18	298	0.105	H-8->LUMO (27%), H-7->LUMO (12%), H-6->L+1 (11%), H-2->LUMO (17%), H-2->L+2 (11%)	0.445837	1.83	26	271	0.1238	H-12->LUMO (22%), H-11->L+1 (20%), H-9->L+1 (11%)	0.365229	1.6
						32	255	0.1164	H-7->L+1 (11%), H-7->L+3 (14%), H-6->L+2 (10%), H-1->L+2 (19%)	0.410384	1.42
R=H											
9	350	0.8665	H-7->L+1 (10%), H-6->LUMO (70%)	0.559309	1.63	13	343	0.7328	H-7->L+1 (10%), H-6->LUMO (60%)	0.524919	1.96
14	321	0.5123	H-7->LUMO (57%), H-6->L+1 (22%)	0.529649	2.07	17	316	0.6058	H-7->LUMO (48%), H-6->L+1 (28%)	0.537067	2.16
16	307	0.296	H-8->LUMO (40%), H-7->L+1 (11%), H-4->L+1 (18%)	0.415832	1.43	21	298	0.2309	H-8->LUMO (23%), H-7->L+1 (24%), H-4->L+1 (34%)	0.386115	1.23
36	253	0.2173	H-10->L+1 (11%), H-7->L+3 (22%), H-6->L+2 (20%), H-2->L+3 (10%)	0.486319	1.03	14	335	0.1826	H-4->LUMO (63%), H-3->LUMO (13%)	0.31023	1.34
10	336	0.1681	H-4->LUMO (62%), H-3->LUMO (18%)	0.341179	1.75	29	264	0.156	H-9->L+1 (10%), H-7->L+3 (13%), H-6->L+2 (18%), HOMO->L+3 (13%)	0.414232	1.13
23	281	0.1182	H-6->L+1 (19%), H-1->L+3 (13%), H-1->L+12 (12%), HOMO->L+2 (10%)	0.462647	1.33	26	271	0.1378	H-12->LUMO (28%), H-11->L+1 (24%)	0.392962	1.65
						32	256	0.1283	H-10->L+1 (10%), H-7->L+1 (11%), H-7->L+3 (14%), H-6->L+2 (11%), H-	0.414667	1.47

									1->L+2 (18%)		
						18	307	0.1224	H-8->LUMO (21%), H-4->L+1 (31%), H-3->L+1 (21%)	0.290866	1.45
R=COOH											
9	359	0.5781	H-6->LUMO (49%), H-2->L+7 (12%)	0.487711	2.13	17	327	0.6173	H-7->LUMO (57%), H-6->L+1 (24%)	0.494755	3.15
13	331	0.537	H-7->LUMO (69%), H-6->L+1 (18%)	0.499959	2.79	18	319	0.2751	H-8->LUMO (33%), H-4->L+1 (27%)	0.342052	1.81
15	316	0.3819	H-8->LUMO (45%), H-7->L+1 (14%), H-4->L+1 (15%)	0.427583	1.81	34	257	0.2646	H-10->L+1 (11%), H-7->L+3 (21%), H-6->L+2 (13%)	0.48178	1.54
16	309	0.2356	H-9->LUMO (42%), H-6->L+1 (17%), H-2->LUMO (16%)	0.449845	2.74	13	355	0.2531	H-10->L+12 (11%), H-6->LUMO (29%)	0.417166	2.56
24	286	0.2315	H-9->LUMO (18%), H-7->LUMO (16%), H-6->L+1 (40%)	0.55932	2.29	11	359	0.1962	H-10->L+12 (12%), H-6->LUMO (24%), H-1->LUMO (11%)	0.390666	2.41
35	256	0.2048	H-7->L+3 (17%), H-6->L+2 (10%), H-1->L+4 (17%), HOMO->L+3 (11%)	0.418941	1.19	25	284	0.1761	H-8->L+1 (15%), H-7->LUMO (21%), H-6->L+1 (33%)	0.519009	2.39
18	304	0.2043	HOMO->L+2 (75%), HOMO->L+4 (10%)	0.30518	0.6	10	366	0.1413	H-10->L+1 (11%), H-6->LUMO (10%), H-2->L+1 (50%)	0.246852	3.1
						31	267	0.1358	H-10->L+1 (10%), H-9->L+1 (10%), H-1->L+2 (27%)	0.281913	1.46
						22	301	0.1356	H-10->LUMO (34%), H-9->LUMO (10%), H-6->L+1 (14%), H-2->LUMO (25%)	0.352428	3.18
						27	275	0.1344	H-12->LUMO (32%), H-11->L+1 (28%)	0.352797	2.22
						20	307	0.1239	H-8->LUMO (12%), H-7->L+1 (13%), H-5->L+1 (13%), H-4->L+1 (49%)	0.289533	1.34
R=NO_2											
8	374	0.3498	H-6->LUMO (60%)	0.439202	3.4	17	339	0.4568	H-7->LUMO (55%), H-6->L+1 (17%)	0.400998	4.21
16	326	0.3469	H-8->LUMO (37%), H-7->L+1 (14%), H-4->L+1 (15%)	0.397524	2.51	39	261	0.3526	H-7->L+3 (22%), H-6->L+4 (14%)	0.499798	1.78
26	296	0.3429	H-9->LUMO (18%), H-7->LUMO (16%), H-6->L+1 (44%)	0.511614	3.2	18	331	0.3062	H-8->LUMO (28%), H-4->L+1 (26%)	0.319444	2.53
13	351	0.3342	HOMO->L+2 (75%)	0.320079	2.66	27	296	0.2839	H-7->LUMO (26%), H-6->L+1 (36%)	0.457669	3.49
19	318	0.2579	H-9->LUMO (45%), H-6->L+1 (20%), H-	0.43355	3.85	12	376	0.2069	H-6->LUMO (21%), H-2->L+1 (28%)	0.2847	3.42

			2->LUMO (16%)	7						93	
12	361	0.1646	H-9->L+7 (17%), H-2->L+7 (35%)	0.413555	1.87	14	372	0.1543	H-6->LUMO (30%), H-2->L+1 (31%)	0.292904	3.83
27	296	0.1243	H-8->LUMO (13%), H-7->L+1 (40%), H-6->LUMO (12%)	0.469789	2.71	26	302	0.1497	H-9->LUMO (45%), HOMO->L+2 (26%)	0.332537	3.05
28	282	0.1188	H-12->LUMO (34%), H-12->L+2 (12%), H-11->L+1 (22%), H-9->L+1 (10%)	0.304091	2.99	35	272	0.134	H-10->L+1 (14%), H-9->L+1 (34%)	0.322129	1.98
34	272	0.1144	H-10->L+1 (27%), HOMO->L+3 (19%)	0.392846	1.57	31	279	0.1239	H-12->LUMO (30%), H-12->L+2 (13%), H-11->L+1 (31%)	0.32404	3.1

Table. S5. Calculated by TD-DFT electronic transitions and their assignment for Ru(III) and Fe(III) complexes. Selected calculated optical transitions with oscillator strengths ($f > 0.1$), wavelengths (λ, nm) and main orbital transition contributions (>10%) H – HOMO, L – LUMO. The selected calculated electron transitions, Λ parameters values and Δr-index for for Ru(III) and Fe(III) complexes by using cam-b3lyp/6-311G(d,p),Lanl2dz level of theory.

No.	λ (nm)	f	Major contribs	Λ	Δr-index, Å	No.	λ (nm)	f	Major contribs	Λ	Δr-index, Å
Ru(III) complex						Fe(III) complex					
R=NH_2											
29	350	0.4305	H-4(A)->LUMO(A) (15%), H-5(B)->L+1(B) (12%), H-1(B)->L+2(B) (30%)	0.38532	2.69	28	338	0.7795	H-4(A)->LUMO(A) (16%), H-5(B)->L+1(B) (21%)	0.446923	2.61
40	324	0.3376	H-2(B)->L+1(B) (62%)	0.313723	2.57	32	328	0.1996	H-4(B)->L+2(B) (10%), H-3(B)->L+2(B) (10%), HOMO(B)->L+1(B) (11%)	0.362869	2.5
33	340	0.3301	H-1(A)->L+1(A) (11%), H-5(B)->L+1(B) (19%), H-1(B)->L+2(B) (25%)	0.359415	2.78	34	324	0.1487	HOMO(B)->L+1(B) (16%), HOMO(B)->L+2(B) (11%)	0.296941	2.49
5	584	0.2478	H-3(B)->LUMO(B) (95%)	0.436768	0.42	33	326	0.1079	HOMO(A)->L+1(A) (13%), HOMO(A)->L+2(A) (23%)	0.302544	2.35
37	328	0.2078	H-3(A)->LUMO(A) (32%), H-5(B)->L+2(B) (14%)	0.512025	2.23	12	504	0.1018	H-6(B)->LUMO(B) (12%), H-3(B)->LUMO(B) (56%), H-1(B)->LUMO(B) (19%)	0.402851	1.06
R=OH						27	342	0.1016	H-1(A)->LUMO(A) (13%), H-8(B)->LUMO(B) (31%)	0.452464	2.23
28	359	0.4302	H-4(A)->LUMO(A) (15%), H-5(B)->L+1(B) (13%), H-4(B)->L+2(B) (11%), H-1(B)->L+2(B) (33%)	0.382162	3.25	R=OH					

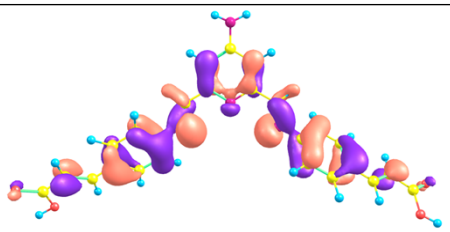
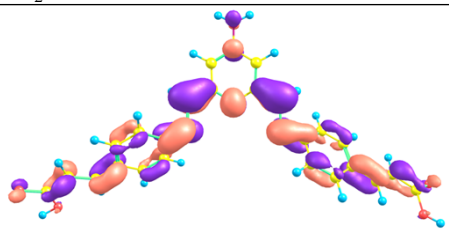
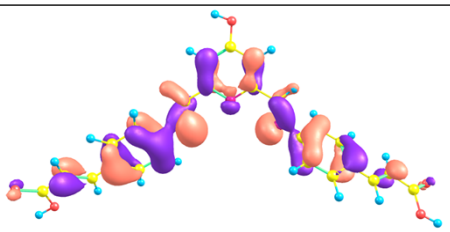
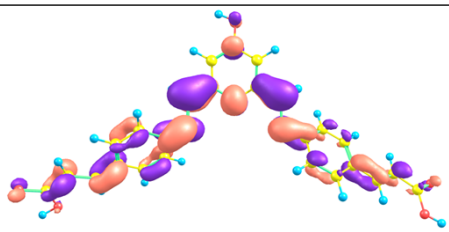
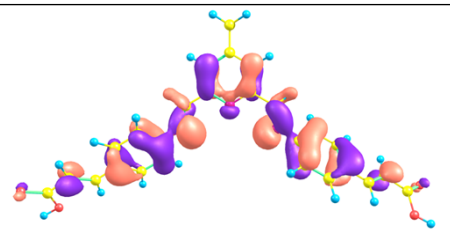
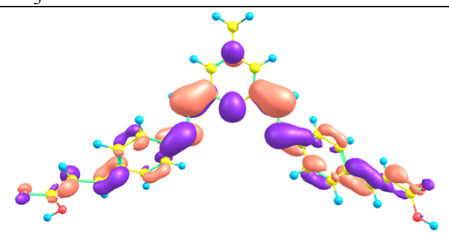
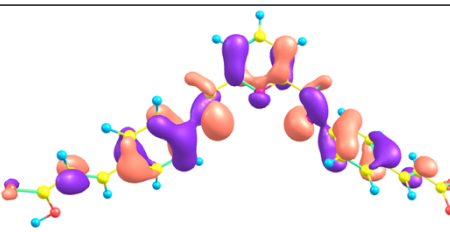
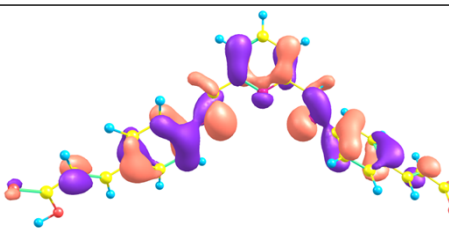
30	350	0.2727	H-1(A)->L+1(A) (12%), H-5(B)->L+1(B) (14%), H-1(B)->L+2(B) (18%)	0.342345	3.04	27	348	0.4258	H-4(A)->LUMO(A) (24%), H-5(B)->L+1(B) (13%), H-2(B)->L+1(B) (10%)	0.374633	2.68
5	618	0.2431	H-3(B)->LUMO(B) (87%)	0.446606	0.54	26	349	0.1675	H-2(A)->LUMO(A) (52%), H-1(A)->LUMO(A) (17%)	0.271537	2.06
39	332	0.1624	H-4(A)->L+1(A) (11%), H-4(B)->L+1(B) (27%)	0.46247	2.98	29	344	0.1309	H-2(B)->L+1(B) (36%)	0.307376	2.45
37	335	0.1324	H-3(A)->LUMO(A) (19%), H-2(B)->L+1(B) (43%)	0.368049	3.04	12	525	0.1269	H-3(B)->LUMO(B) (59%), H-1(B)->LUMO(B) (21%)	0.410237	1.22
R=CH_3											
27	359	0.6747	H-3(A)->LUMO(A) (21%), H-4(B)->L+1(B) (24%), H-1(B)->L+2(B) (13%)	0.451021	3.36	27	352	0.4844	H-4(A)->LUMO(A) (19%), H-4(B)->L+1(B) (11%), H-2(B)->L+1(B) (18%)	0.381268	2.7
36	338	0.3485	H-4(A)->LUMO(A) (40%), H-5(B)->L+1(B) (11%), H-4(B)->L+2(B) (12%)	0.462334	3.14	29	347	0.1579	H-5(A)->LUMO(A) (16%), H-2(B)->L+1(B) (11%)	0.347293	2.4
5	631	0.2619	H-3(B)->LUMO(B) (94%)	0.459232	0.45	12	530	0.1352	H-6(B)->LUMO(B) (10%), H-3(B)->LUMO(B) (60%), H-1(B)->LUMO(B) (18%)	0.420755	1.28
39	328	0.1199	H-6(A)->LUMO(A) (21%), H-5(B)->L+1(B) (17%)	0.396026	2.47						
R=H											
27	363	0.6712	H-3(A)->LUMO(A) (23%), H-5(B)->L+2(B) (10%), H-4(B)->L+1(B) (31%), H-1(B)->L+2(B) (10%)	0.461993	2.5	27	356	0.3238	H-2(A)->LUMO(A) (11%), H-5(B)->L+1(B) (18%), H-2(B)->L+1(B) (24%)	0.362037	2.45
4	646	0.2728	H-3(B)->LUMO(B) (96%)	0.467323	0.39	10	546	0.153	H-3(B)->LUMO(B) (45%), H-1(B)->LUMO(B) (18%)	0.397595	1.87
34	342	0.1674	H-4(A)->LUMO(A) (29%), HOMO(A)->L+1(A) (12%), H-2(B)->L+1(B) (23%)	0.386635	2.47	28	354	0.1295	H-3(A)->LUMO(A) (12%), H-2(B)->L+1(B) (18%), HOMO(B)->L+1(B) (10%)	0.337078	2.78
38	331	0.1434	H-6(A)->LUMO(A) (71%)	0.327611	1.5						
R=COOH											
25	375	0.2791	H-4(A)->LUMO(A) (15%), H-2(B)->L+1(B) (22%)	0.368646	3.65	31	362	0.4406	H-4(A)->LUMO(A) (14%), H-5(B)->L+1(B) (20%), H-4(B)->L+1(B) (16%)	0.41245	3.04
4	684	0.2413	H-3(B)->LUMO(B) (87%)	0.484719	0.36	36	345	0.1645	H-7(A)->LUMO(A) (34%), H-6(A)->LUMO(A) (11%)	0.386072	2.36
27	372	0.1999	H-3(B)->L+1(B) (18%), H-2(B)->L+1(B) (31%)	0.335246	3.17	11	559	0.1624	H-3(B)->LUMO(B) (62%), H-1(B)->LUMO(B) (10%)	0.42965	1.43
36	348	0.138	H-7(A)->LUMO(A) (10%), H-6(A)-	0.2824	2.46	R=NO_2					

		3	>LUMO(A) (51%)	01								
24	378	0.1162	HOMO(B)->L+2(B) (44%)	0.334601	2.34	38	358	0.2036	H-7(A)->LUMO(A) (26%), H-6(A)->LUMO(A) (22%)	0.34664	3.08
R=NO_2						33	373	0.1969	H-5(B)->L+1(B) (40%), H-1(B)->L+1(B) (11%)	0.378314	3.62
27	387	0.3462	H-5(A)->LUMO(A) (21%), H-5(B)->L+1(B) (20%), H-2(B)->L+1(B) (12%)	0.387237	4.5	35	369	0.1873	H-6(B)->L+1(B) (16%), H-4(B)->L+1(B) (32%)	0.334957	3.67
4	718	0.2679	H-3(B)->LUMO(B) (90%)	0.50508	0.58	10	582	0.127	H-3(B)->LUMO(B) (51%)	0.418201	1.67

Table S6. Calculated redox potential and dipole moment of the ruthenium and iron-based complexes.

Ligand substituents	Hammett constants	Redox potential V vs NHE	Dipole moment, debye	Redox potential V vs NHE	Dipole moment, debye
		Ru		Fe	
NH_2	-0.66	0.46	14.2	0.54	11.30
OH	-0.37	0.60	11.2	0.64	9.47
CH_3	-0.17	0.64	11.4	0.67	10.55
H	0	0.67	10.3	0.79	9.02
COOH	0.45	0.76	9.4	0.96	9.22
NO_2	0.78	0.86	8.2	0.86	7.8

Table S7 Representation of Natural transition orbitals (NTO) of the Hole and Electron (particle) pair for most intensive electron excitations of diphormylpyridile Schiff base ligand systems. NTO pairs that contribute more than 50% to each excited state (Isodensity contour 0.03).

Excited state	Hole	Electron	Hole-electron eigenvalue
R=NH_2			
1			0.5848
R=OH			
1			0.5880
R=CH_3			
1			0.6278
R=H			
1			0.6362

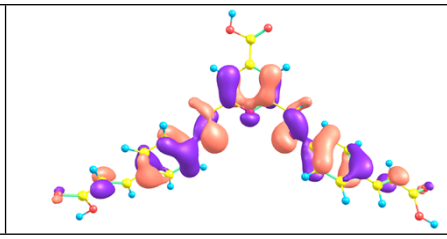
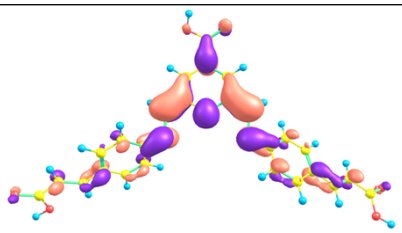
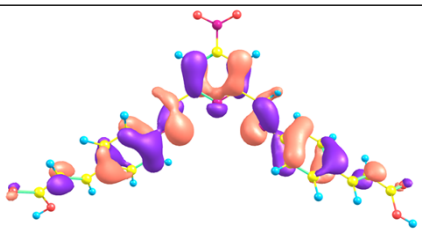
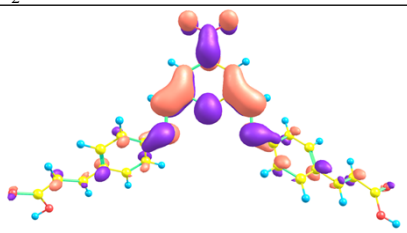
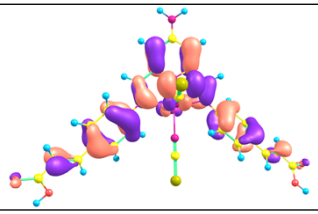
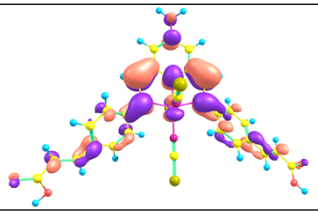
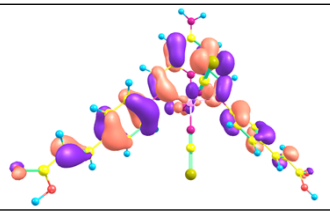
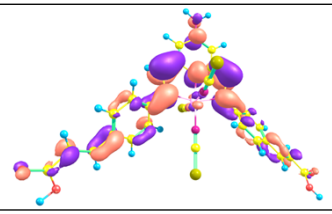
R=COOH			
1			0.6885
R=NO_2			
1			0.7359

Table S8 Representation of Natural transition orbitals (NTO) of the Hole and Electron (particle) pair for most intensive electron excitations of Ru(II) and Fe(II) complexes. NTO pairs that contribute more than 50% to each excited state (Isodensity contour 0.03).

Excited state	Hole	Electron	Hole-electron eigenvalue	Excited state	Hole	Electron	Hole-electron eigenvalue
Ru(II)-complexes				Fe(II)-complexes			
R=NH_2							
10			0.6941	13			0.6271
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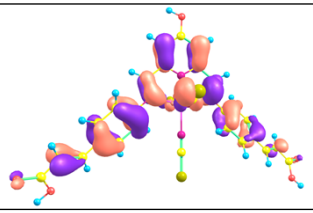
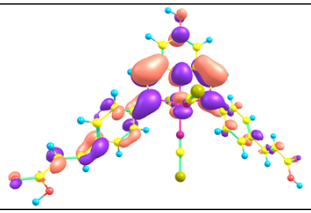
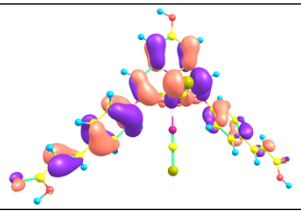
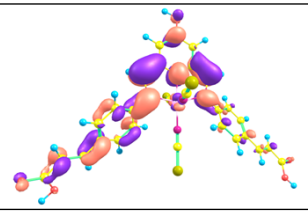
9			0.6784	13			0.6372
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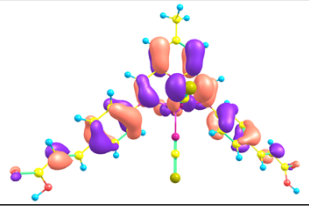
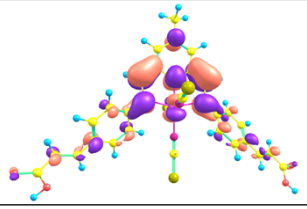
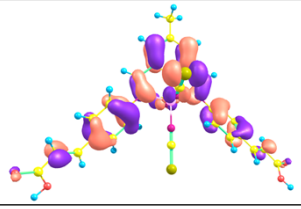
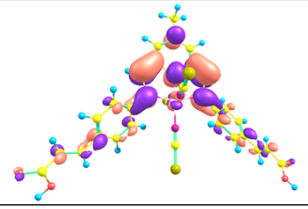
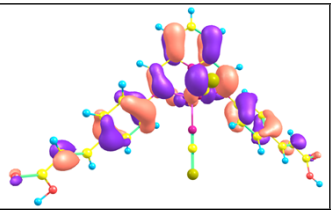
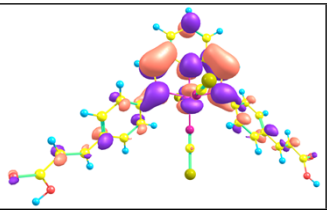
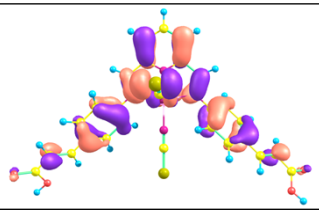
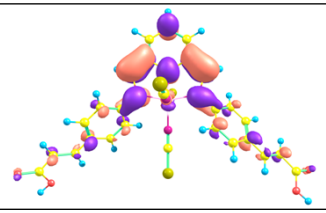
9			0.7562	13			0.6949
R=H							
9			0.7635	13			0.7045

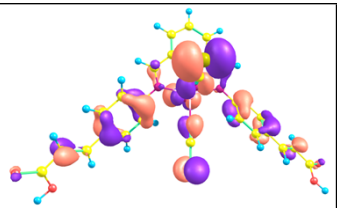
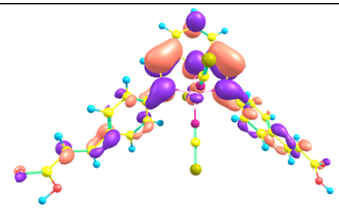
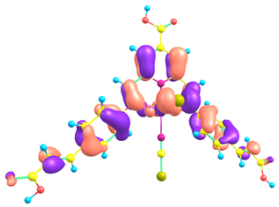
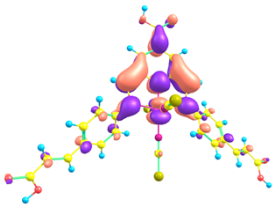
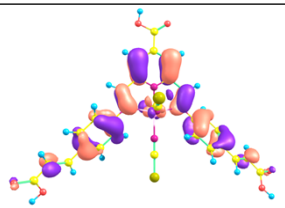
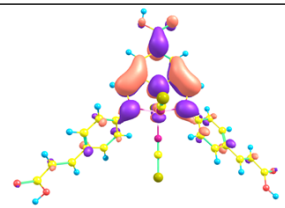
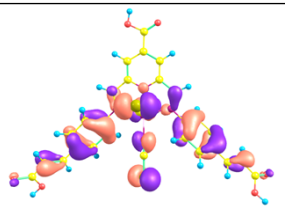
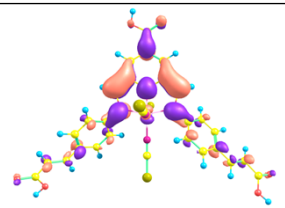
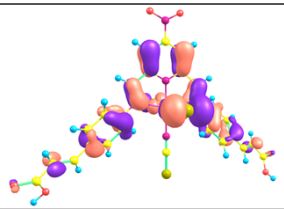
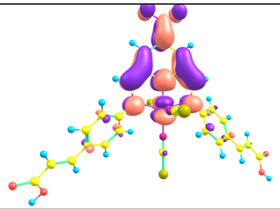
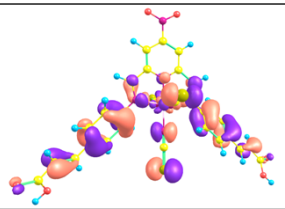
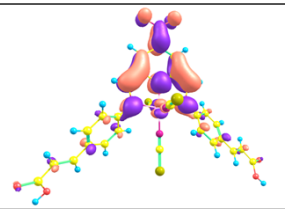
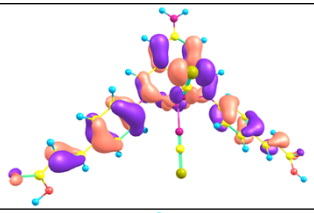
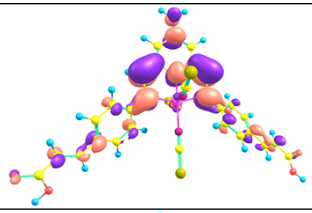
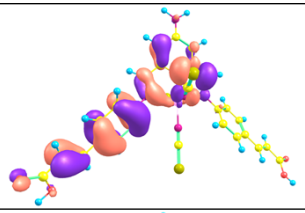
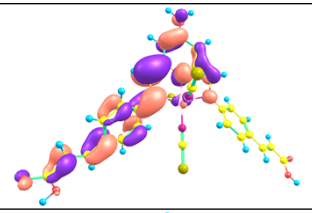
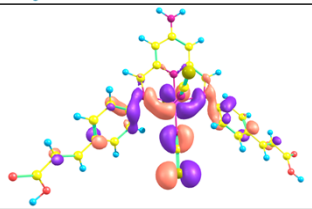
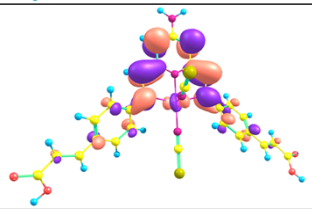
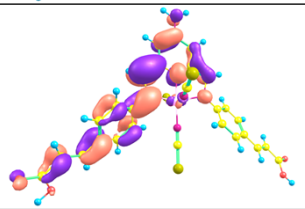
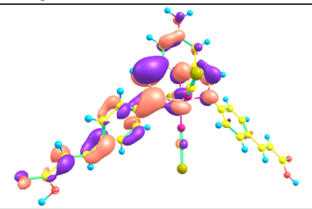
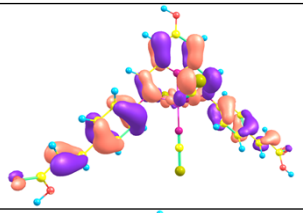
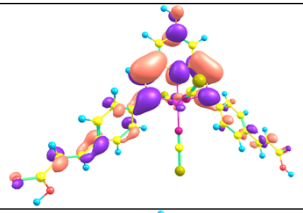
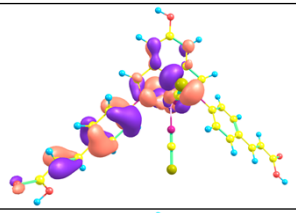
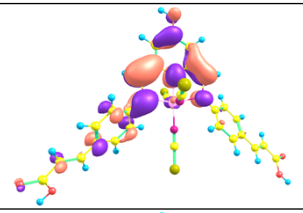
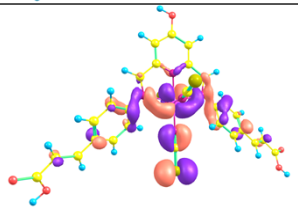
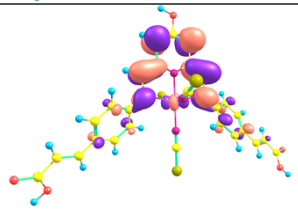
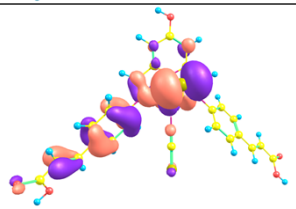
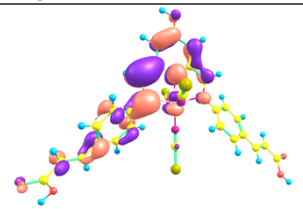
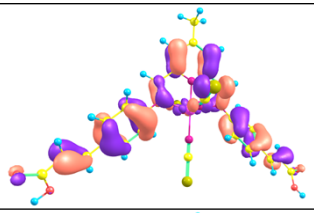
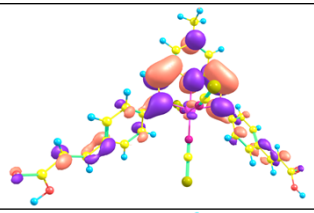
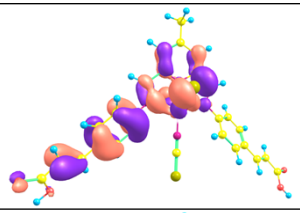
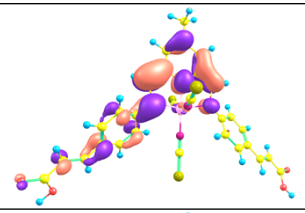
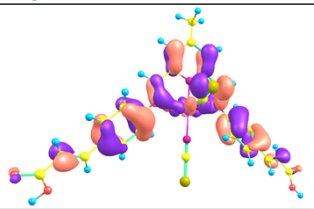
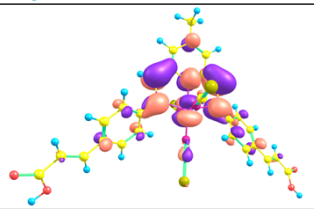
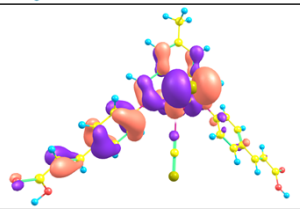
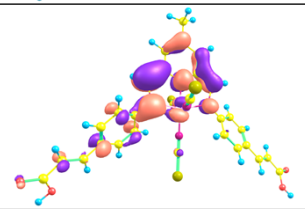
				17			0.6589
R=COOH							
9			0.5492	13			0.3456
				17			0.7039
R=NO_2							
8			0.8203	17			0.7273

Table S9. Representation of Natural transition orbitals (NTO) of the Hole and Electron (particle) pair for most intensive electron excitations of Ru(III) and Fe(III) complexes. NTO pairs that contribute more than 20% to each excited state (Isodensity contour 0.03).

Excited state	Hole	Electron	Hole-electron	Excited state	Hole	Electron	Hole-electron

			eigenvalue				eigenvalue
Ru(III)-complexes				Fe(III)-complexes			
R=NH_2							
29			A 0.3518	28			A 0.6610
			B 0.9403				B 0.7404
R=OH							
28			A 0.3482	27			A 0.8623
			B 1.0905				B 0.7945
R=CH_3							

27			A 0.4966	27			A 0.6837
			B 0.6823				B 1.0112
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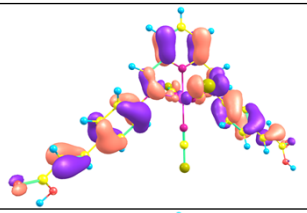
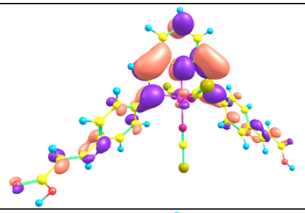
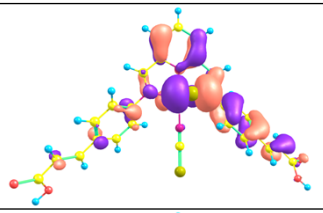
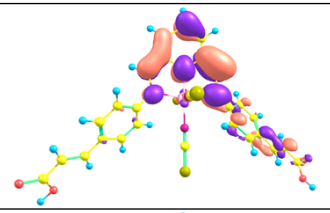
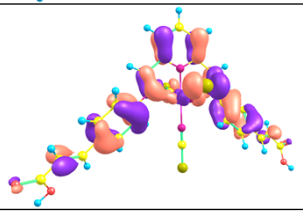
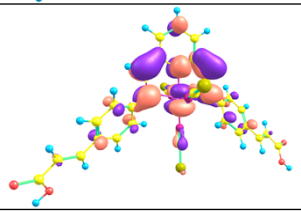
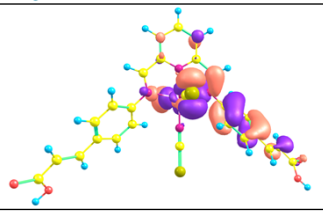
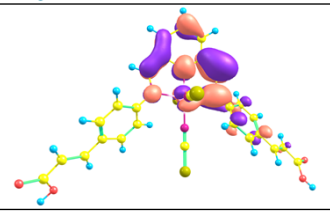
27			A 0.4978	27			A 0.4798
			B 0.7424				B 1.1891
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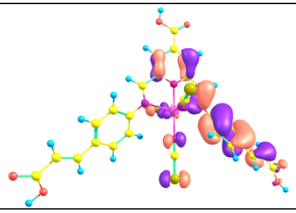
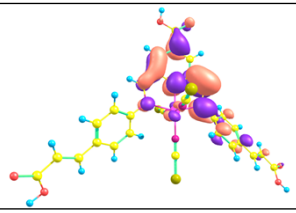
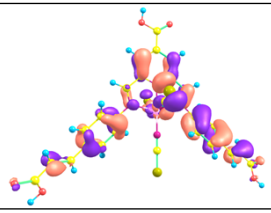
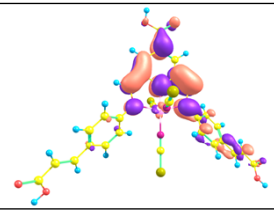
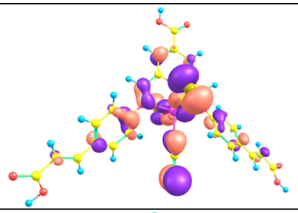
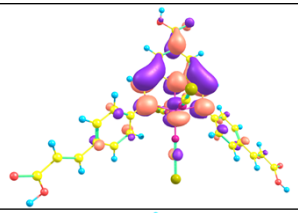
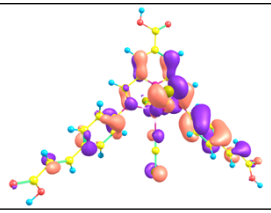
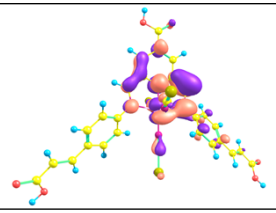
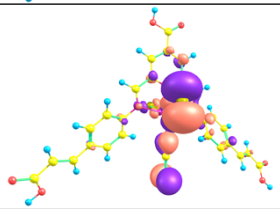
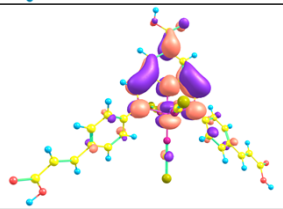
25			A 0.4066	31			A 0.4813

			B 0.8765				B 1.044
27			B 1.3930				
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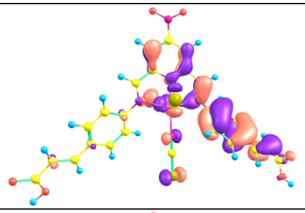
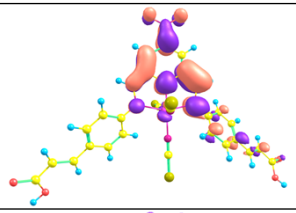
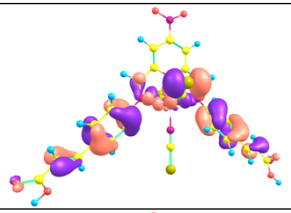
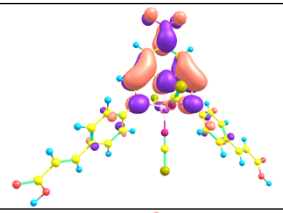
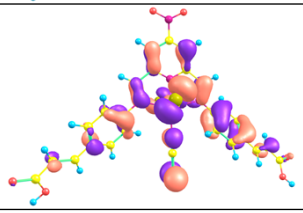
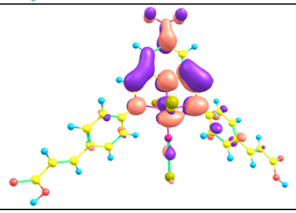
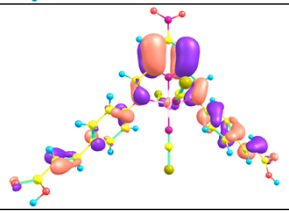
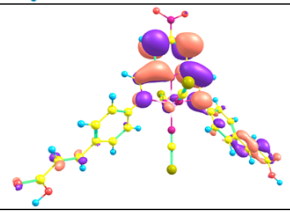
27			A 0.53854	38			A 1.3328
			B 0.9349				B 0.2477