inorganics

MDPI

Supplementary Materials: Synthesis of a Ru(II) Complex with a Naphthoquinone-Annelated Imidazole Ligand Exhibiting Proton-Responsive Redox and Luminescent Behavior

Takuya Shiga *, Minami Tachibana, Hiroki Oshio and Masayuki Nihei

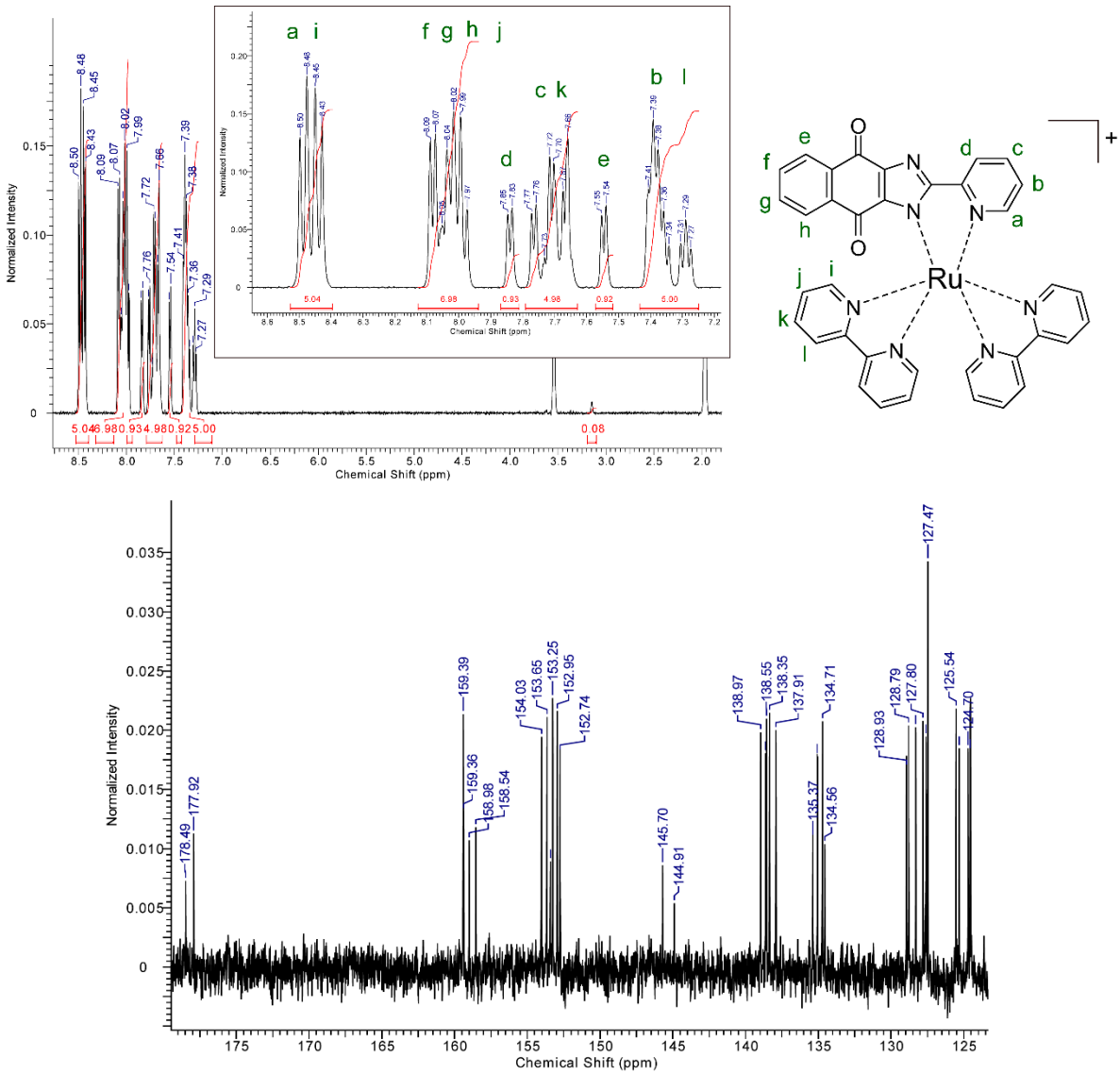

Figure S1. ^{1}H and ^{13}C NMR spectra of **1** in CD_3CN-d_3.

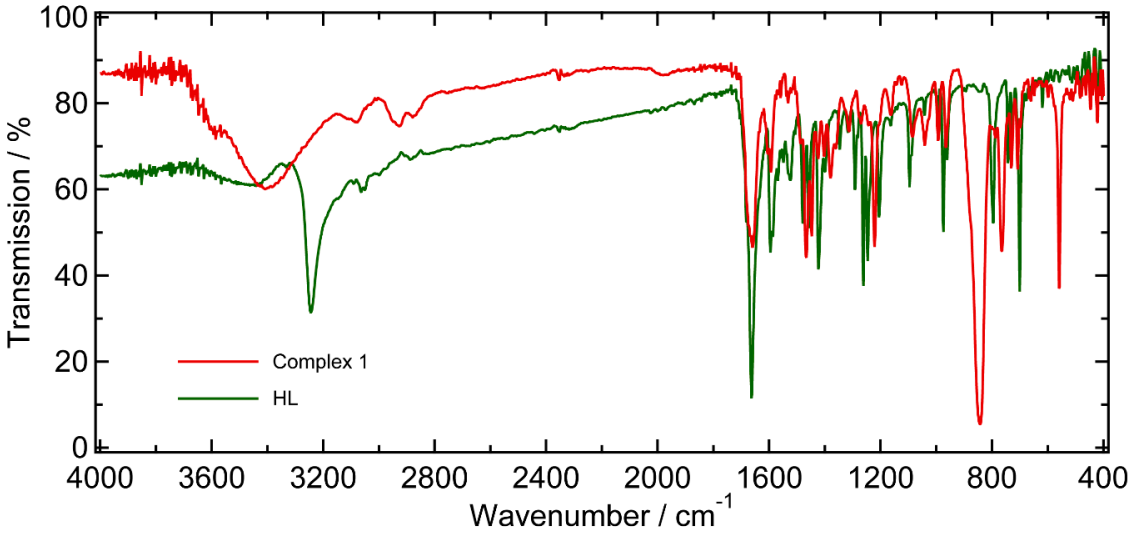

Figure S2. IR spectra of HL (green) and complex **1** (red).

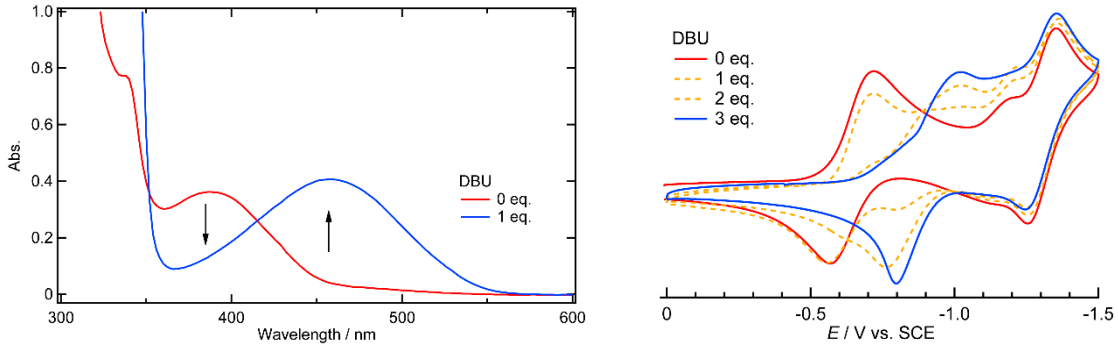

Figure S3. UV-Vis absorption spectra of HL and L^- in DMF (left) and cyclic voltammograms of HL and L^- in CH_2Cl_2 (left).

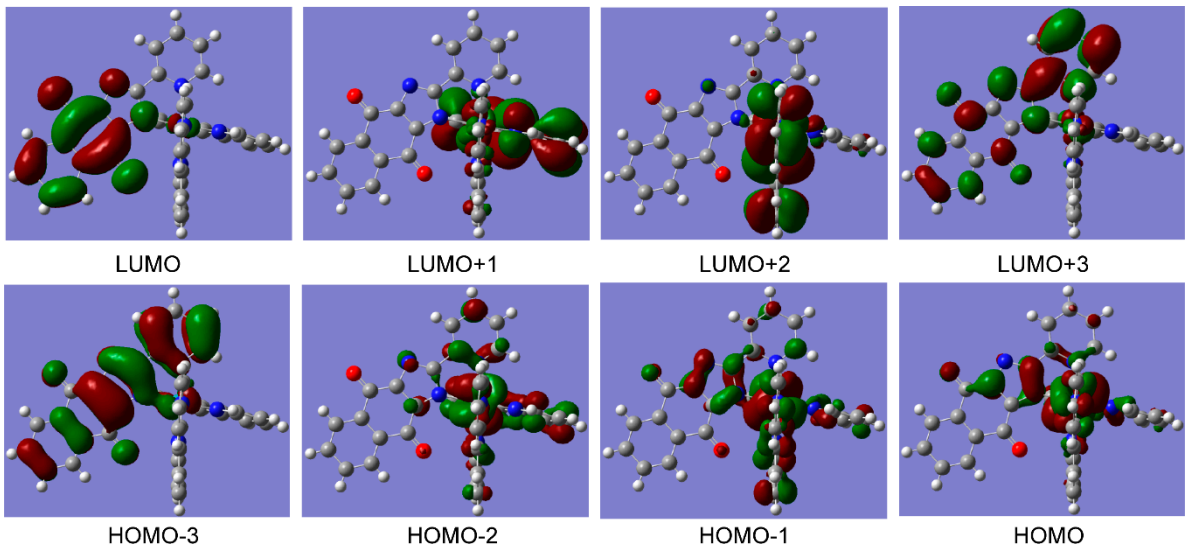

Figure S4. Calculated frontier orbitals for the optical transitions observed in **1**. Orbitals are shown with an iso-value of 0.06.

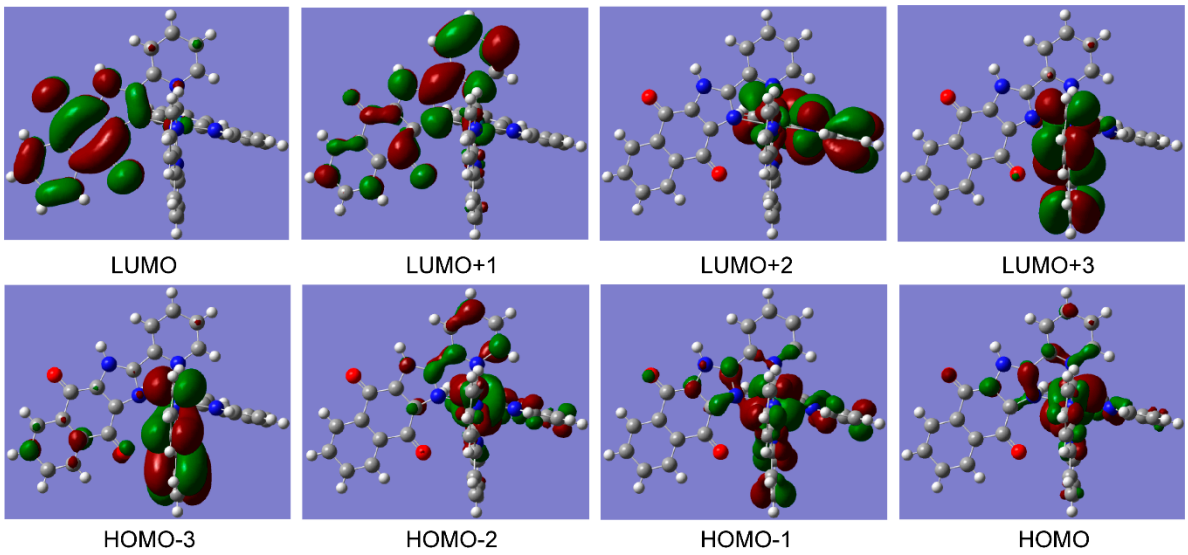

Figure S5 Calculated frontier orbitals for the optical transitions observed in H^+-**1**. Orbitals are shown with an iso-value of 0.06.

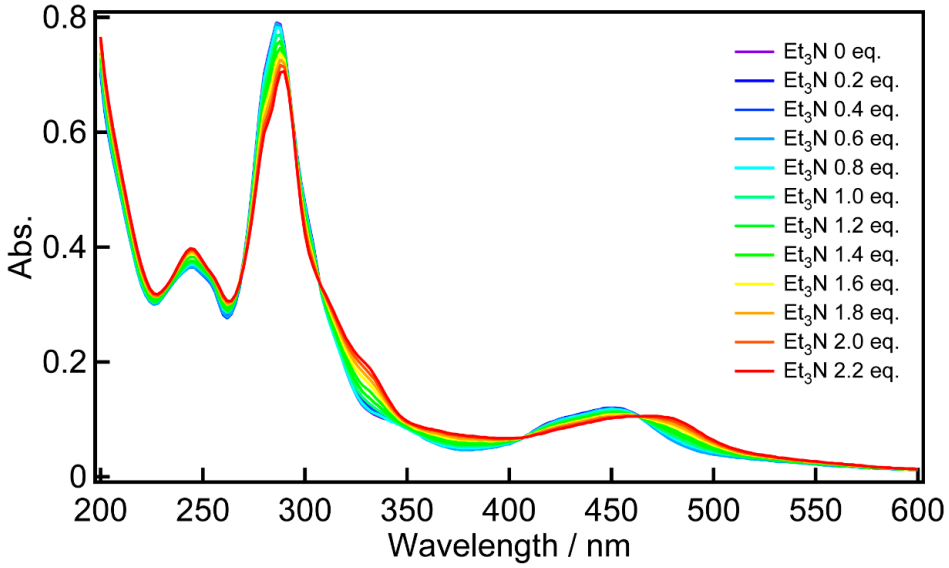

Figure S6 UV-Vis absorption spectral changes of complex **1** with Et_3N after addition of 1.6 eq. TfOH.

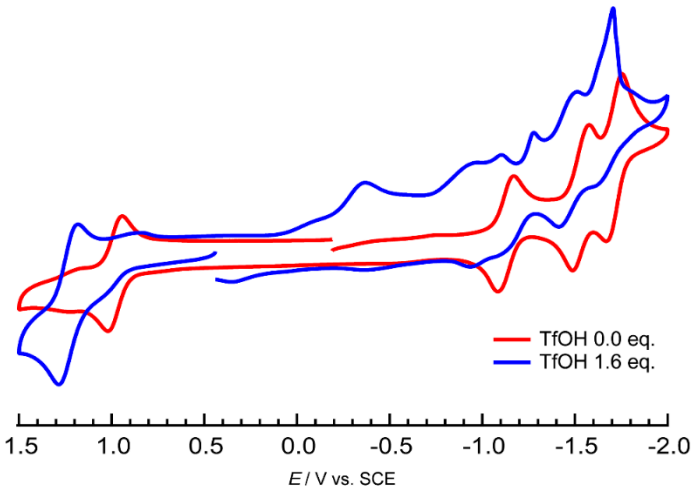

Figure S7 Cyclic voltammograms of complex **1** in acetonitrile before and after the addition of 1.6 eq. of TfOH.

Table S1. Main TD-DFT calculated transition of **1** compared with experimental data.

Main contributing excitation	Transition wavelength (nm)	Oscillator strength	Exp. Transition Wavelength (nm)	
HOMO-2 → LUMO	529.28	0.0419	478	MLCT Ru/L^-
HOMO-1 → LUMO				MLCT Ru/L^-
HOMO → LUMO				MLCT Ru/L^-
HOMO-2 → LUMO+1	525.73	0.0477	478	MLCT Ru/L^-
HOMO-2 → LUMO+2				MLCT Ru/ L^-
HOMO-2 → LUMO+1	434.32	0.0659	450 sh	MLCT Ru/bpy
HOMO-2 → LUMO+2				MLCT Ru/bpy
HOMO → LUMO+3				MLCT Ru/bpy
HOMO-2 → LUMO+1	428.01	0.0814	450 sh	MLCT Ru/bpy
HOMO-2 → LUMO+2				MLCT Ru/bpy
HOMO-1 → LUMO+1				MLCT Ru/bpy
HOMO-1 → LUMO+2				MLCT Ru/bpy

Table S2. Main TD-DFT calculated transition of H^+-**1** compared with experimental data.

Main contributing excitation	Transition wavelength (nm)	Oscillator strength	Exp. Transition Wavelength (nm)	
HOMO-2 → LUMO	618.90	0.0577	450	MLCT Ru/HL
HOMO-1 → LUMO				MLCT Ru/HL
HOMO → LUMO				MLCT Ru/bpy
HOMO-2 → LUMO+1	437.37	0.1160	420 sh	MLCT Ru/HL
HOMO-2 → LUMO+2				MLCT Ru/bpy
HOMO-1 → LUMO+1				MLCT Ru/HL
HOMO-1 → LUMO+3				MLCT Ru/bpy
HOMO-2 → LUMO+2	404.02	0.1399	420 sh	MLCT Ru/bpy
HOMO-2 → LUMO+3				MLCT Ru/bpy
HOMO-1 → LUMO+2				MLCT Ru/bpy
HOMO-1 → LUMO+3				MLCT Ru/bpy

Table S3. Cartesian coordinates of geometry optimized **1**.

Atom	Coordinates in Å		
	X	Y	Z
Ru	1.043811	0.032108	0.156844
N	1.431936	1.954103	0.846293
N	-0.883348	0.762074	0.425296
N	-2.131872	2.591533	0.988671
N	0.9052	-0.814998	2.009796
N	0.604818	-1.905391	-0.333538
N	2.977999	-0.47849	-0.287126
N	1.237523	0.815902	-1.726633
O	-2.194748	-1.754261	-0.709211
O	-5.036776	2.708934	0.591073
C	2.643705	2.519956	0.95891
H	3.410195	2.000205	0.751175
C	2.819498	3.825193	1.365032
H	3.69086	4.202138	1.405518
C	1.709412	4.578956	1.713031
H	1.809755	5.474313	2.015925
C	0.46125	4.008063	1.609448
H	-0.312893	4.502082	1.847015
C	0.34751	2.708354	1.155386
C	-0.925545	2.047097	0.916324
C	-2.196053	0.479152	0.170898
C	-2.824371	-0.723007	-0.390956
C	-4.28945	-0.633924	-0.612691
C	-4.949416	-1.74627	-1.159732
H	-4.453657	-2.528993	-1.374404
C	-6.294773	-1.715738	-1.387568
H	-6.734425	-2.474305	-1.754433
C	-7.019568	-0.581523	-1.081792
H	-7.952925	-0.562231	-1.251294
C	-6.404092	0.521768	-0.536806
H	-6.915093	1.294643	-0.328309
C	-5.041531	0.508943	-0.290493
C	-4.36305	1.713293	0.300727
C	-2.970381	1.614179	0.50484
C	1.046423	-0.161792	3.197376
H	1.341019	0.74166	3.194947
C	0.771853	-0.765985	4.397865

H	0.863466	-0.280759	5.209289
C	0.366453	-2.07393	4.418258
H	0.166062	-2.500226	5.244087
C	0.24871	-2.7652	3.238093
H	-0.022382	-3.676051	3.243571
C	0.531481	-2.130666	2.03015
C	0.411548	-2.75747	0.700212
C	0.120484	-4.090408	0.504041
H	-0.056163	-4.655748	1.248746
C	0.083077	-4.59643	-0.770619
H	-0.081862	-5.519648	-0.920447
C	0.289611	-3.745515	-1.823953
H	0.250964	-4.068172	-2.717508
C	0.561045	-2.401699	-1.574763
H	0.716385	-1.819221	-2.308668
C	3.827472	-1.194811	0.506251
H	3.542419	-1.433687	1.380796
C	5.070905	-1.581297	0.093722
H	5.650847	-2.038837	0.691774
C	5.475601	-1.306922	-1.186346
H	6.330887	-1.58561	-1.491235
C	4.616364	-0.610906	-2.033943
H	4.865531	-0.439023	-2.934128
C	3.398674	-0.176553	-1.55304
C	2.440805	0.617299	-2.332985
C	2.718064	1.192015	-3.560503
H	3.561895	1.050131	-3.971016
C	1.76425	1.970213	-4.189182
H	1.939262	2.35275	-5.04119
C	0.563687	2.182805	-3.564577
H	-0.097023	2.730286	-3.972463
C	0.313518	1.599652	-2.341334
H	-0.523453	1.749677	-1.918795

Table S4 Cartesian coordinates of geometry optimized H^+-**1**.

Atom	Coordinates in Å		
	X	Y	Z
Ru	1.050209	0.029731	0.154466
N	1.426702	1.962166	0.820792
N	-0.881345	0.752391	0.410829
N	-2.140759	2.58179	0.949623
N	0.91314	-0.795236	2.017494
N	0.622601	-1.916034	-0.312699
N	2.987886	-0.475704	-0.280095
N	1.242773	0.791318	-1.738217
O	-2.177119	-1.784864	-0.694668
O	-5.045596	2.678387	0.545979
C	2.635179	2.535986	0.928359
H	3.404836	2.017918	0.728267
C	2.803179	3.847068	1.318643
H	3.672404	4.229246	1.355869
C	1.688424	4.598974	1.655557
H	1.78338	5.498529	1.947552
C	0.443567	4.020027	1.557028
H	-0.333653	4.512691	1.787254
C	0.337668	2.714221	1.118838
C	-0.931363	2.043113	0.885914
C	-2.192064	0.459178	0.157845
C	-2.812884	-0.75323	-0.390151
C	-4.278056	-0.674902	-0.615302
C	-4.931038	-1.797496	-1.149644
H	-4.430663	-2.580078	-1.353862
C	-6.276161	-1.777135	-1.379983
H	-6.711061	-2.542557	-1.738171
C	-7.007637	-0.643223	-1.089364
H	-7.940802	-0.631128	-1.260578
C	-6.399091	0.470047	-0.557036
H	-6.914644	1.242624	-0.358895
C	-5.036891	0.467714	-0.308412
C	-4.36597	1.682948	0.269001
C	-2.973122	1.593977	0.476538
C	1.048827	-0.126691	3.197156
H	1.338496	0.77826	3.184063
C	0.775561	-0.717547	4.404562

H	0.863179	-0.221871	5.210089
C	0.377265	-2.027341	4.440427
H	0.177829	-2.444524	5.271126
C	0.265253	-2.733726	3.268685
H	-0.000877	-3.645911	3.284956
C	0.546567	-2.112579	2.053465
C	0.432263	-2.756361	0.731164
C	0.148797	-4.093188	0.550972
H	-0.026003	-4.650271	1.302305
C	0.116267	-4.615066	-0.717413
H	-0.043388	-5.540948	-0.856114
C	0.319907	-3.776071	-1.780824
H	0.284505	-4.109914	-2.670395
C	0.583597	-2.427822	-1.547782
H	0.736978	-1.853585	-2.288561
C	3.839934	-1.17754	0.523404
H	3.554734	-1.407184	1.40037
C	5.086139	-1.562268	0.117651
H	5.667572	-2.009227	0.722221
C	5.491458	-1.301468	-1.165054
H	6.348757	-1.579205	-1.465122
C	4.629848	-0.620655	-2.022533
H	4.879569	-0.458511	-2.92437
C	3.409011	-0.187082	-1.548962
C	2.448125	0.59185	-2.340157
C	2.724286	1.152914	-3.574221
H	3.569558	1.010604	-3.981609
C	1.767288	1.918079	-4.213963
H	1.941627	2.291046	-5.07034
C	0.564548	2.131774	-3.593939
H	-0.098459	2.670566	-4.009594
C	0.315531	1.562371	-2.364002
H	-0.522946	1.713005	-1.944679
H	-2.390674	3.496103	1.26833