Electronic Supplementary Information for:

Simultaneous control of spectroscopic and electrochemical properties in ECL active tris(2,2′-bipyridine)ruthenium(II) derivatives containing chemical attachment functionality

Gregory J. Barbante, Conor F. Hogan*, David J. D. Wilson, Naomi A. Lewcenko, Frederick M. Pfeffer, Neil W. Barnett and Paul S. Francis*

Table S1. Comparison of HOMO - LUMO gap (H-L) calculated by DFT and time dependant (TD) DFT with experimental data for the $[Ru(bpy)_2(L)]^{2+}$ complexes in acetonitrile.

Complex number	TD-DFT H-L / eV	DFT H-L / eV	ΔE^o (II - I)[a] / eV	Photoluminescence λ_{max} / eV	Absorbance λ_{max} / eV
0	2.74	3.81	2.65	2.01	2.75
7	2.70	3.78	2.59	1.98	2.77
1	2.70	3.78	2.59	1.97	2.73
6	2.71	3.78	2.59	1.97	2.73
4	2.33	3.44	2.43	1.86	2.64
2	2.38	3.50	2.49	1.85	2.68
3	2.43	3.54	2.38	1.81	2.59
5	2.47	3.58	2.38	1.81	2.59

Table S2. Compound 0. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.54	4	96	
LUMO+5	-1.61	3	97	
LUMO+4	-1.61	3	97	
LUMO+3	-1.95	1	99	
LUMO+2	-2.59	4	96	
LUMO+1	-2.59	4	96	
LUMO	-2.71	2	98	
HOMO	-6.50	80	20	
HOMO-1	-6.67	76	24	
HOMO-2	-6.67	76	24	
HOMO-3	-7.80	0	100	
HOMO-4	-7.80	0	100	

Table S3. Compound 1. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.50	4	91	5
LUMO+5	-1.52	2	52	46
LUMO+4	-1.59	3	96	1
LUMO+3	-1.90	1	79	20
LUMO+2	-2.52	3	15	81
LUMO+1	-2.57	4	95	1
LUMO	-2.68	2	83	15
HOMO	-6.43	79	13	8
HOMO-1	-6.58	75	12	13
HOMO-2	-6.61	75	20	4
HOMO-3	-7.73	1	8	91
HOMO-4	-7.78	0	99	0

Table S4. Compound 2. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.66	3	97	0
LUMO+5	-1.83	2	87	12
LUMO+4	-2.29	0	13	87
LUMO+3	-2.52	2	0	98
LUMO+2	-2.66	4	95	1
LUMO+1	-2.72	3	96	1
LUMO	-3.20	5	2	92
HOMO	-6.68	79	14	7
HOMO-1	-6.85	76	20	4
HOMO-2	-6.86	74	12	13
HOMO-3	-7.85	0	99	0
HOMO-4	-7.88	1	97	2

Table S5. Compound 3. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.65	3	97	0
LUMO+5	-1.82	2	84	14
LUMO+4	-2.24	0	15	84
LUMO+3	-2.43	2	0	98
LUMO+2	-2.65	4	95	1
LUMO+1	-2.71	3	95	2
LUMO	-3.13	5	3	92
HOMO	-6.65	79	14	7
HOMO-1	-6.82	76	20	4
HOMO-2	-6.83	75	12	13
HOMO-3	-7.84	0	99	0
HOMO-4	-7.87	1	96	3

Table S6. Compound 4. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.78	3	97	0
LUMO+5	-1.90	2	77	21
LUMO+4	-2.24	1	25	74
LUMO+3	-2.50	2	2	97
LUMO+2	-2.80	5	93	1
LUMO+1	-2.85	4	93	3
LUMO	-3.23	5	4	90
HOMO	-6.65	73	18	9
HOMO-1	-6.86	70	25	5
HOMO-2	-6.86	69	15	16
HOMO-3	-7.58	0	0	99
HOMO-4	-7.69	0	0	100

Table S7. Compound 5. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.64	3	97	0
LUMO+5	-1.80	2	81	17
LUMO+4	-2.19	0	19	81
LUMO+3	-2.35	2	0	98
LUMO+2	-2.64	4	95	1
LUMO+1	-2.71	3	95	2
LUMO	-3.07	5	3	92
HOMO	-6.63	79	14	7
HOMO-1	-6.80	76	20	4
HOMO-2	-6.81	75	12	13
HOMO-3	-7.84	0	99	0
HOMO-4	-7.87	1	95	4

Table S8. Compound 6. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.50	4	89	8
LUMO+5	-1.56	3	43	55
LUMO+4	-1.59	3	94	3
LUMO+3	-1.91	1	75	24
LUMO+2	-2.54	4	19	77
LUMO+1	-2.58	4	95	1
LUMO	-2.68	2	80	19
HOMO	-6.45	79	13	8
HOMO-1	-6.60	75	12	13
HOMO-2	-6.63	76	20	4
HOMO-3	-7.75	1	12	88
HOMO-4	-7.79	0	99	0

Table S9. Compound 7. Mulliken population analysis of frontier molecular orbitals.

Orbital	Energy (eV)	% Ru	% bpy	% ligand
LUMO+6	-1.50	3.7	91	6
LUMO+5	-1.53	2	47	50
LUMO+4	-1.59	3	95	2
LUMO+3	-1.90	1	78	21
LUMO+2	-2.51	3	12	84
LUMO+1	-2.57	4	95	1
LUMO	-2.67	2	86	12
HOMO	-6.43	79	13	8
HOMO-1	-6.59	75	12	14
HOMO-2	-6.61	75	20	4
HOMO-3	-7.01	0	0	100
HOMO-4	-7.72	1	7	93