On the Viability of Cyclometalated Ru(II) Complexes as Dyes in DSSC Regulated by COOH Group, A DFT Study

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Supplementary Information

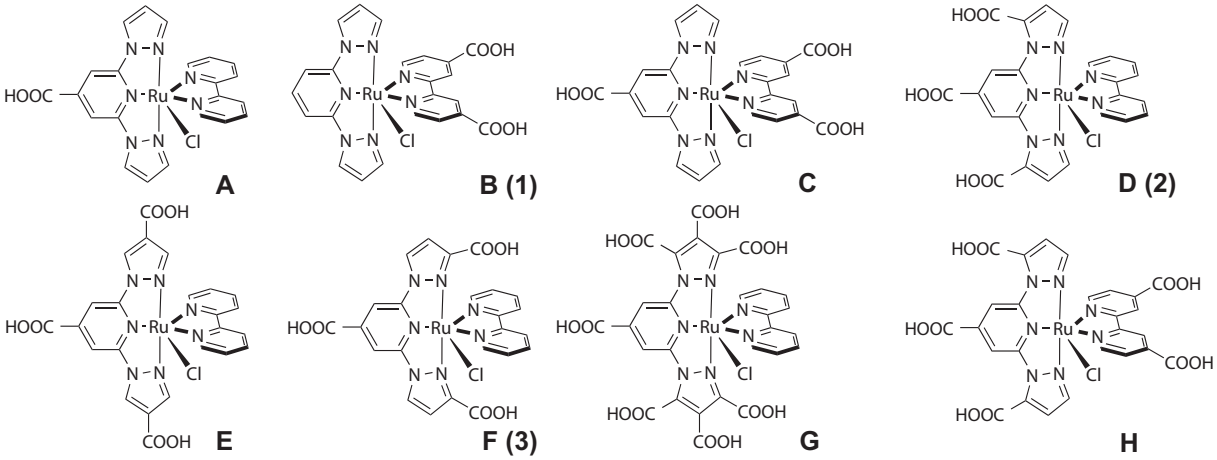

Figure ESI-1 The possible conformations been tested in current investigation.

1 The Possible Conformations

All possible conformations been tested in the current investigation are listed in Figure ESI-1. Note that the "possible conformation" mentioned here are related to those could exist from the perspective of computational chemistry, rather than that of all possible structures from a point view of mathematica. The screening procedure based on the following two facts: more absorption peaks and higher driving force as compared with the experimentally explored complex **1**. The screening details are also described in detail in the text.

2 FMO Data

For **1**, the resultant 4d composition from the population analysis is 67.2% for HOMO, 66.5% for HOMO - 1 and 68.6% for HOMO - 2. While HOMO - 6 is localized on the bpy ligand. The character of the virtual orbitals are complicated. LUMO + 3 is dominated by bpy ligand. LUMO and LUMO +1 are contributed from p-orbital of COOH groups while the LUMO + 7 is characterized as 4d(Ru) perturbed by bpy and bpp ligands.

For **2**, the listed virtual orbitals are all dominated by the bpp ligand except LUMO + 2 which is mainly populated by bpy ligand. The top two occupied orbitals of **2** are 4d(Ru) character but combined with contributions from bpp ligand (in HOMO) or from both bpp and Cl atom (in HOMO - 1). The other interested occupied orbitals HOMO - 5 and HOMO - 6 are totally localized on ligands, as shown in Table ESI-1.

For **3**, the compositions of the concerned frontier molecular orbitals are similar as those of **2**, in which the virtual orbitals are controlled by the bpp ligand while the occupied orbitals are composed by the metal and ligands.

Table ESI-1 Frontier molecular orbital compositions for **1**, **2**, and **3**

Complex	Orbital	Main Component (%)					Energy (eV)
		Ru	bpp	bpy	Cl	COOH[a]	
1	137 (LUMO + 7)	45.9	19.1	26.3	8.5	0.2	-0.66
	133 (LUMO + 3)	0.3	0.9	90.6	0.0	8.2	-2.19
	131 (LUMO + 1)	1.8	1.2	66.7	0.1	30.2	-2.64
	130 (LUMO)	7.7	3.3	73.9	0.2	14.9	-3.13
				$\lvert\Delta E(HOMO-LUMO)\rvert$			2.71
	129 (HOMO)	67.2	15.4	7.5	9.1	0.8	-5.84
	128 (HOMO - 1)	66.5	11.9	8.6	13.0	0.1	-6.09
	127 (HOMO - 2)	68.6	17.1	13.0	0.0	1.3	-6.36
	123 (HOMO - 6)	0.3	0.4	98.4	0.2	0.6	-7.64
2	144 (LUMO + 3)	0.5	60.7	1.0	0.1	37.7	-2.53
	143 (LUMO + 2)	5.3	5.7	88.2	0.1	0.7	-2.59
	142 (LUMO + 1)	3.4	72.2	4.2	0.0	20.2	-2.89
	141 (LUMO)	8.2	70.8	2.0	1.0	18.0	-3.27
				$\lvert\Delta E(HOMO-LUMO)\rvert$			2.76
	140 (HOMO)	65.4	16.1	6.2	10.1	2.2	-6.03
	139 (HOMO - 1)	63.2	14.7	6.5	13.9	1.6	-6.26
	135 (HOMO - 5)	2.0	86.5	0.4	9.9	1.2	-7.55
	134 (HOMO - 6)	10.6	16.1	9.6	62.7	1.0	-7.67
3	143 (LUMO + 2)	0.7	61.5	1.1	0.1	36.6	-2.43
	142 (LUMO + 1)	3.5	76.7	2.7	0.0	17.0	-2.80
	141 (LUMO)	8.8	69.3	2.1	0.8	19.0	-3.24
				$\lvert\Delta E(HOMO-LUMO)\rvert$			2.74
	140 (HOMO)	67.5	14.2	6.6	10.7	0.9	-5.98
	139 (HOMO - 1)	64.0	14.5	6.6	13.1	1.9	-6.20
	135 (HOMO - 5)	2.1	81.7	0.4	9.9	5.9	-7.59

[a] The COOH components are not included into the related bpp or bpy ligand.