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Supporting Information

Non-Innocence of 1,4-Dicyanamidobenzene Bridging Ligands in Dinuclear Ruthenium Complexes.

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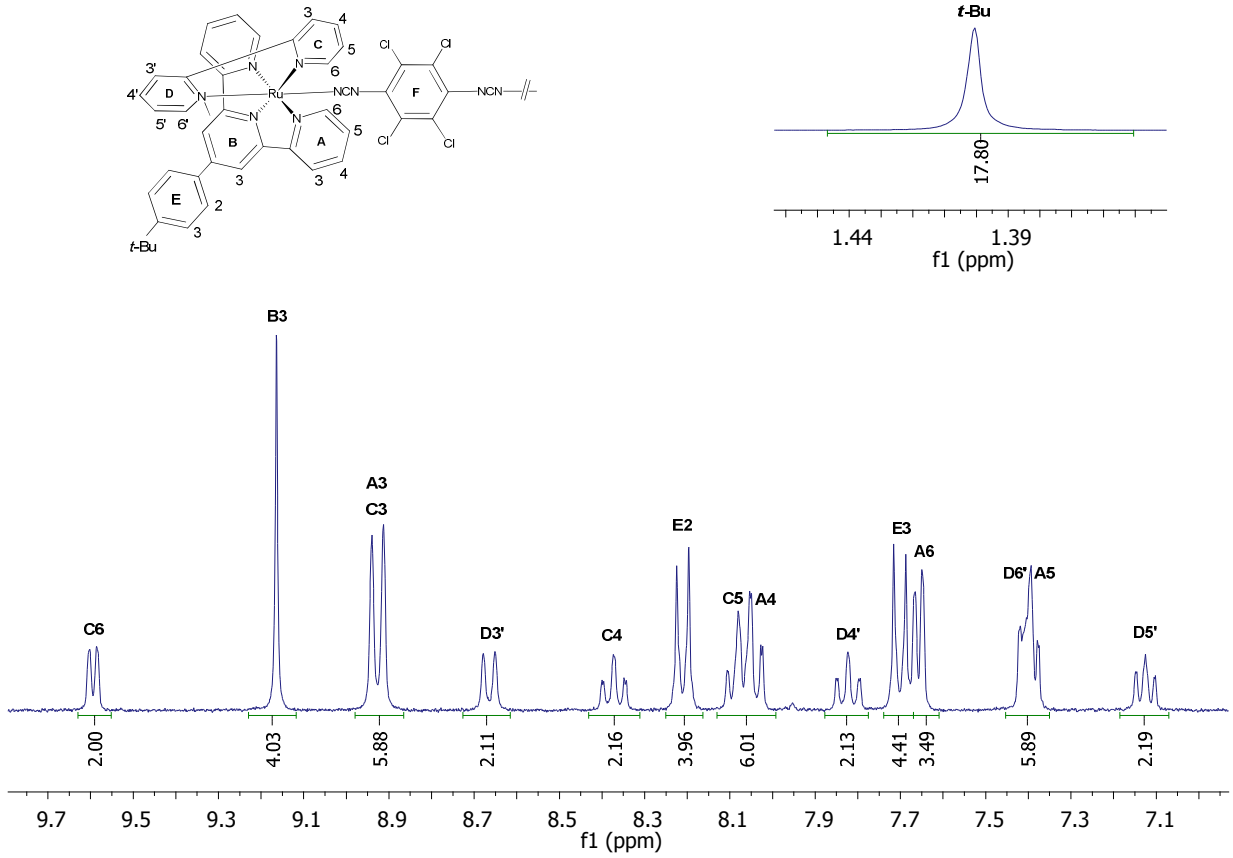

Figure S1 ^{1}H NMR of complex **4** in DMSO-d_6

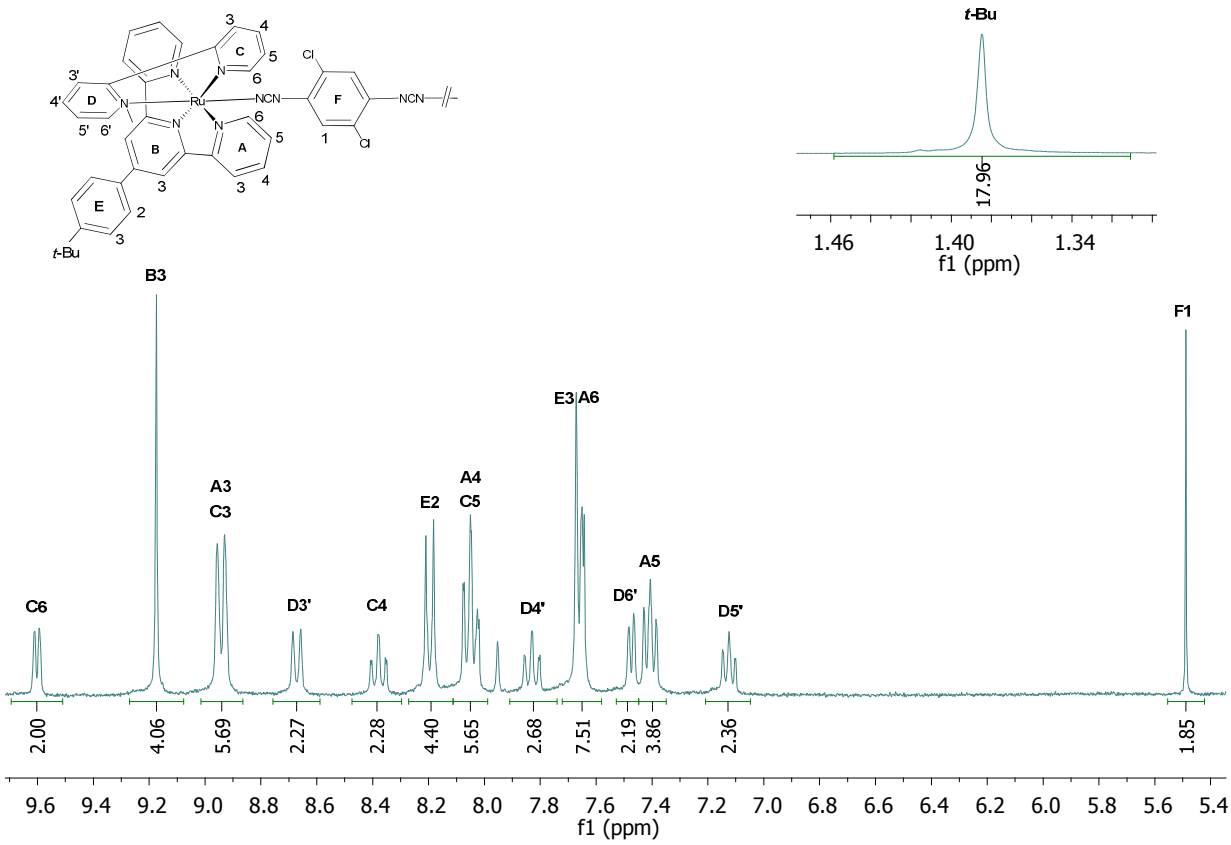

Figure S2 ^{1}H NMR of complex **3** in DMSO-d_6

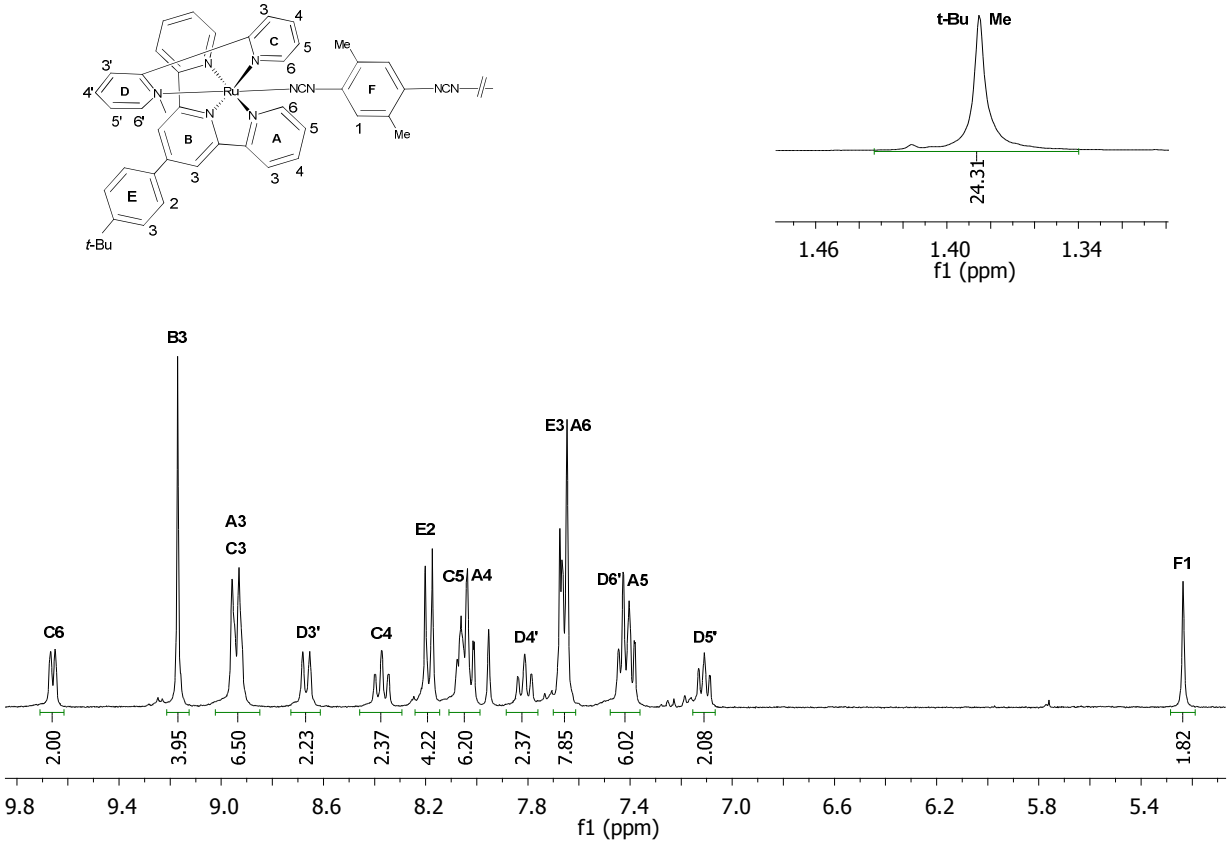

Figure S3 ^{1}H NMR of complex **1** in DMSO-d_6

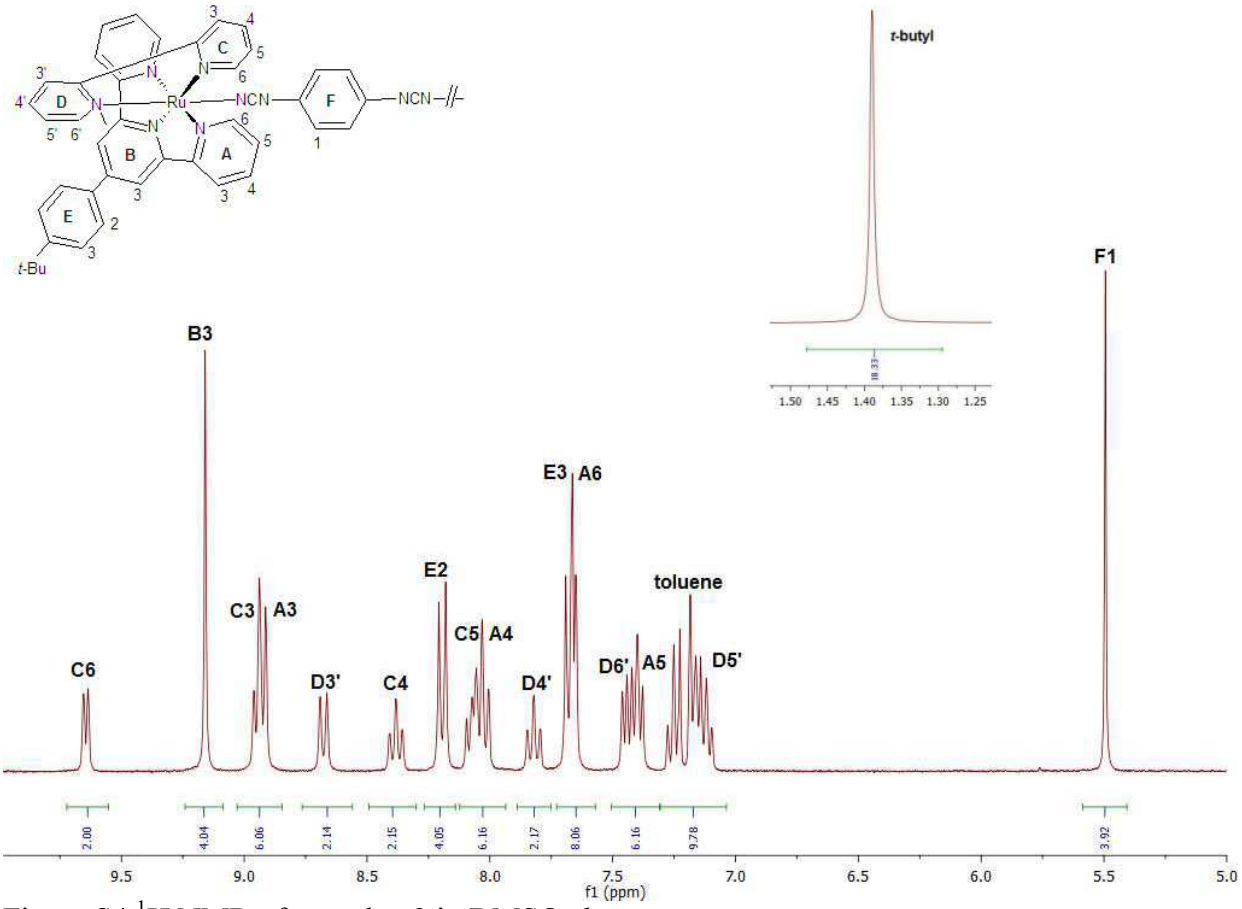

Figure S4 ^{1}H NMR of complex **2** in DMSO-d_6

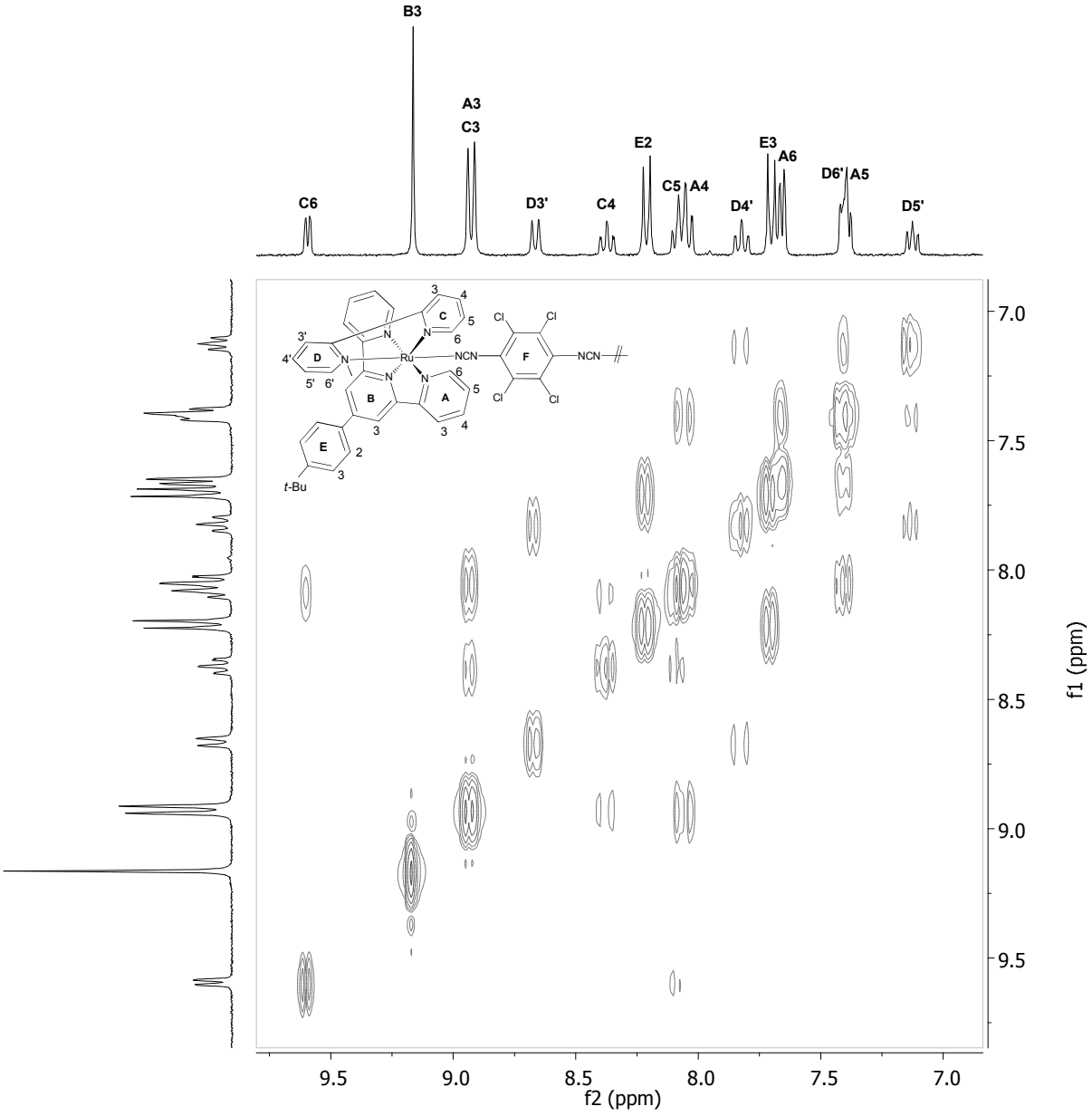

Figure S5 COESY experiment for complex **4** in DMSO-d_6

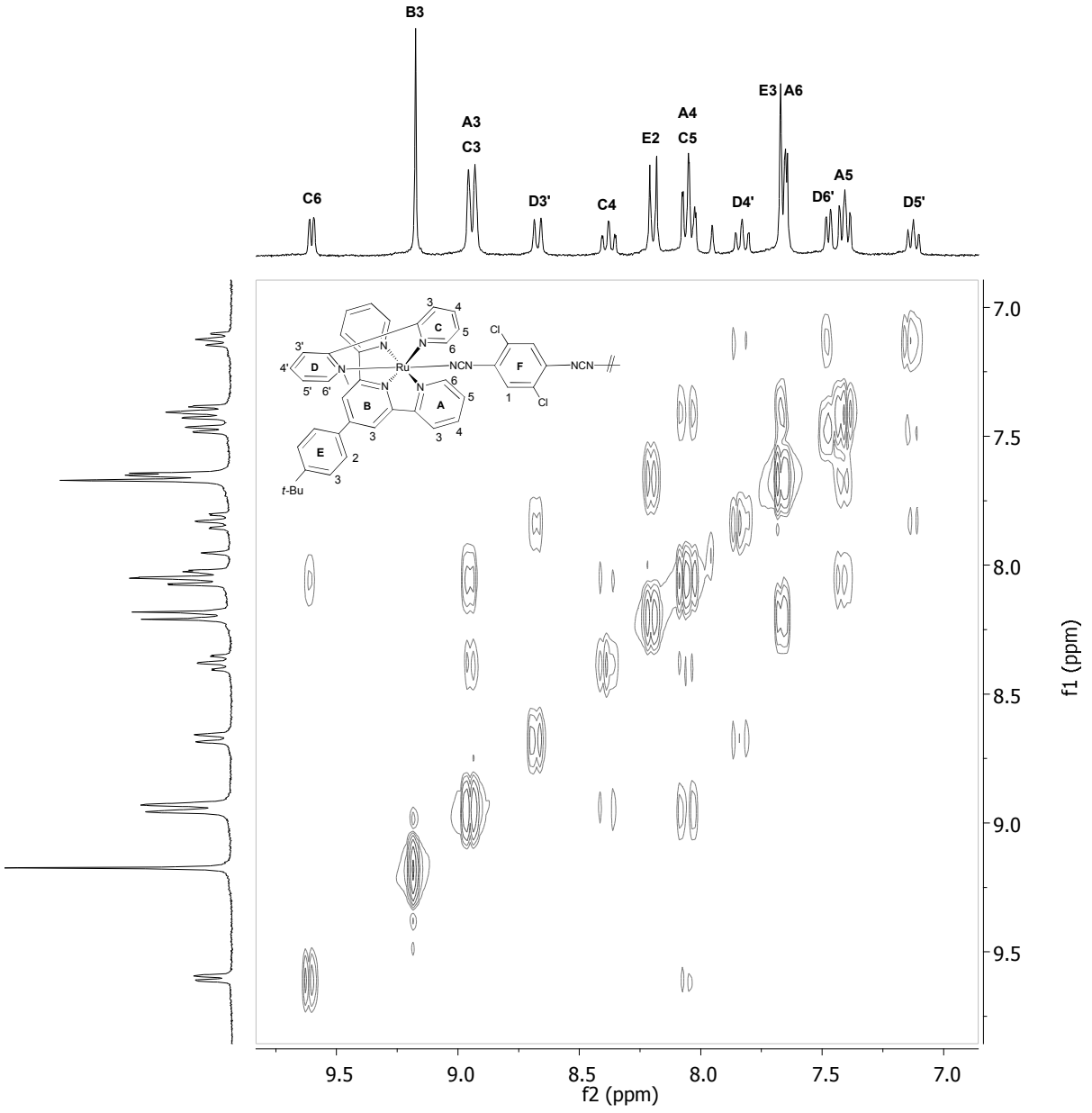

Figure S6 COESY experiment for complex **3** in DMSO-d_6

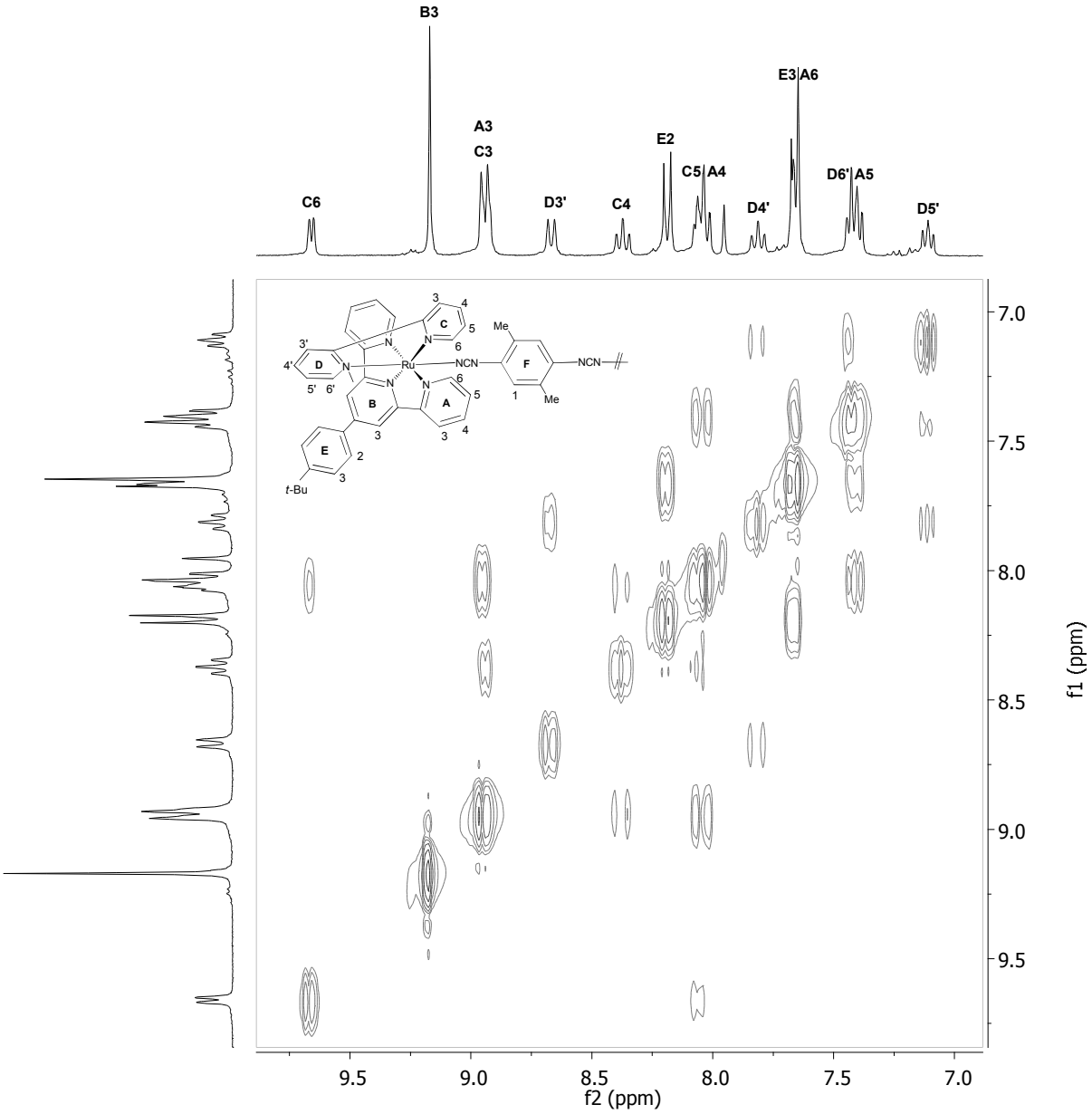

Figure S7 COESY experiment for complex **1** in DMSO-d_6

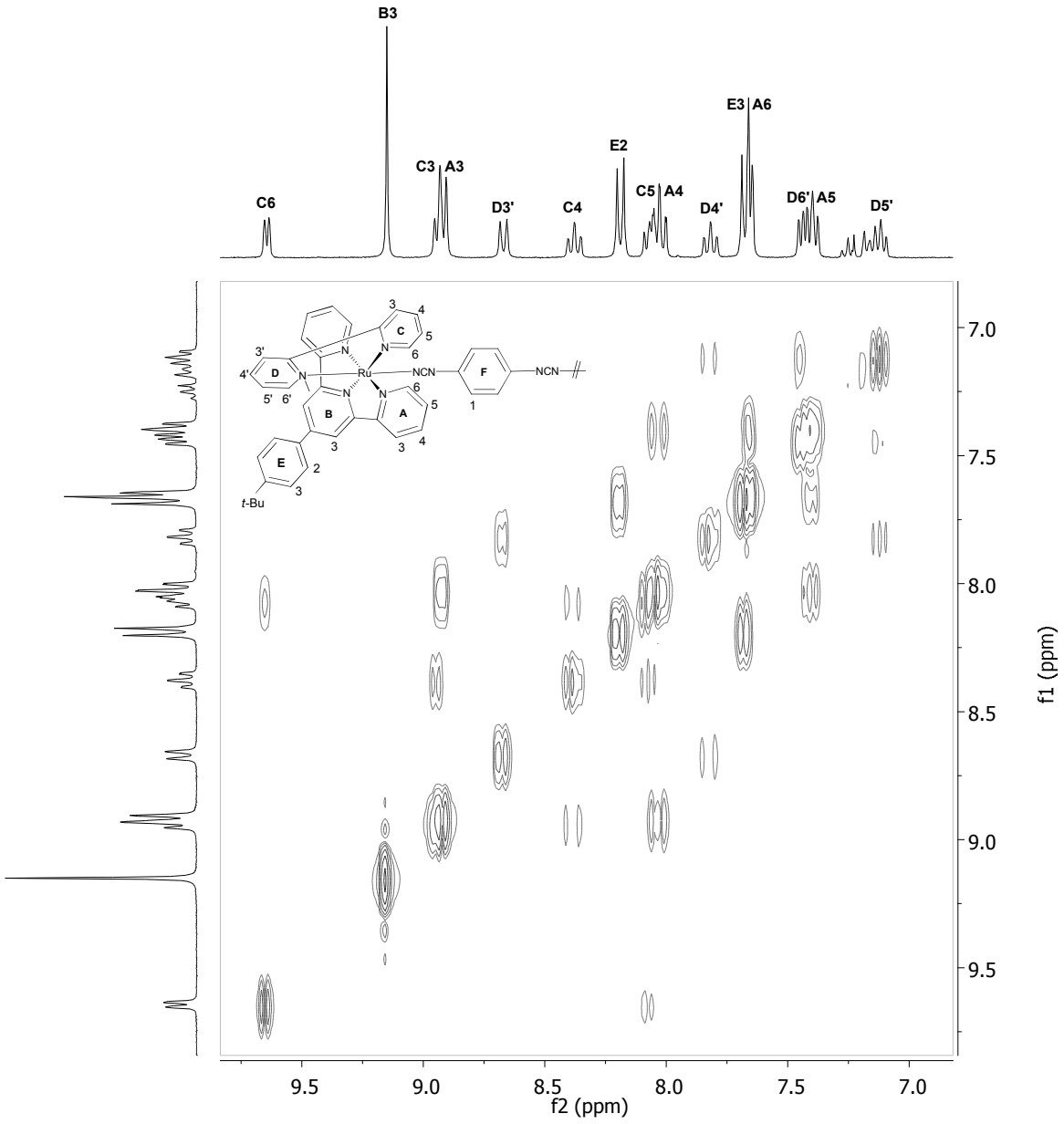

Figure S8 COESY experiment for complex **2** in DMSO-d_6

Table S1. H NMR data of complexes 1-4 in DMSO-d_6

Complexes	Chemical Shift (ppm)/type	*J* values (Hz)
[{Ru(ttpy)(bpy)}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_2$	9.66 (d, 2H) (**C6**)	5.2
	9.17 (s, 4H) (**B3**)	
	8.94 (d, 6H) (**C3, A3**)	8.0
	8.67 (d, 2H) (**D3'**)	8.3
	8.37 (t, 2H) (**C4**)	7.9
	8.19 (d, 4H) (**E2**)	8.5
	8.08-8.01 (m, 6H) (**C5, A4**)	
	7.81 (t, 2H) (**D4'**)	8.3
	7.68-7.64 (m, 8H) (**E3, A6**)	
	7.44-7.38 (m, 6H) (**D6', A5**)	
	7.11 (t, 2H) (**D5'**)	6.7
	5.24 (s, 2H) (**F1**)	
	1.39 (s, 24H) (***t*-Bu, Me**)	
[{Ru(ttpy)(bpy)}$_2$(μ-dicyd)][PF$_6$]$_2$	9.64 (d, 2H) (**C6**)	5.2
	9.15 (s, 4H) (**B3**)	
	8.95-8.91 (m, 6H) (**C3, A3**)	
	8.67 (d, 2H) (**D3'**)	8.2
	8.38 (t, 2H) (**C4**)	7.9
	8.19 (d, 4H) (**E2**)	8.5
	8.11 – 7.97 (m, 6H) (**C5, A4**)	
	7.82 (t, 2H) (**D4'**)	7.9
	7.69-7.65 (m, 8H) (**E3, A6**)	
	7.48 – 7.34 (m, 6H) (**D6', A5**)	
	7.12 (t, 2H) (**D5'**)	7.2
	5.49 (s, 4H) (**F1**)	
	1.39 (s, 18H) (***t*-Bu**)	
[{Ru(ttpy)(bpy)}$_2$(μ-Cl$_2$dicyd)][PF$_6$]$_2$	9.60 (d, 2H) (**C6**)	4.9
	9.17 (s, 4H) (**B3**)	
	8.94 (d, 6H) (**C3, A3**)	7.9
	8.67 (d, 2H) (**D3'**)	8.2
	8.38 (t, 2H) (**C4**)	7.2
	8.20 (d, 4H) (**E2**)	8.5
	8.08-8.02 (m, 6H) (**C5, A4**)	
	7.83 (t, 2H) (**D4'**)	8.5
	7.67-7.64 (m, 8H) (**E3, A6**)	
	7.47 (d, 2H) (**D6'**)	5.1
	7.41 (t, 4H) (**A5**)	6.9
	7.12 (t, 2H) (**D5'**)	6.6
	5.49 (s, 2H) (**F1**)	
	1.38 (s, 18H) (***t*-Bu**)	

[{Ru(ttpy)(bpy)}$_2$(μ-Cl$_4$dicyd)][PF$_6$]$_2$	9.59 (d, 2H) (**C6**) 9.16 (s, 4H) (**B3**) 8.93 (d, 6H) (**C3, A3**) 8.66 (d, 2H) (**D3'**) 8.37 (t, 2H) (**C4**) 8.21 (d, 4H) (**E2**) 8.10-8.02 (m, 6H) (**C5, A4**) 7.82 (t, 2H) (**D4'**) 7.70 (d, 4H) (**E3)** 7.66 (d, 4H) (**A6**) 7.45 – 7.35 (m, 6H) (**D6', A5**) 7.13 (t, 2H) (**D5'**) 1.40 (s, 18H) (***t*-Bu**)	5.1 8.2 8.3 8.0 8.5 8.5 8.5 4.8 7.1

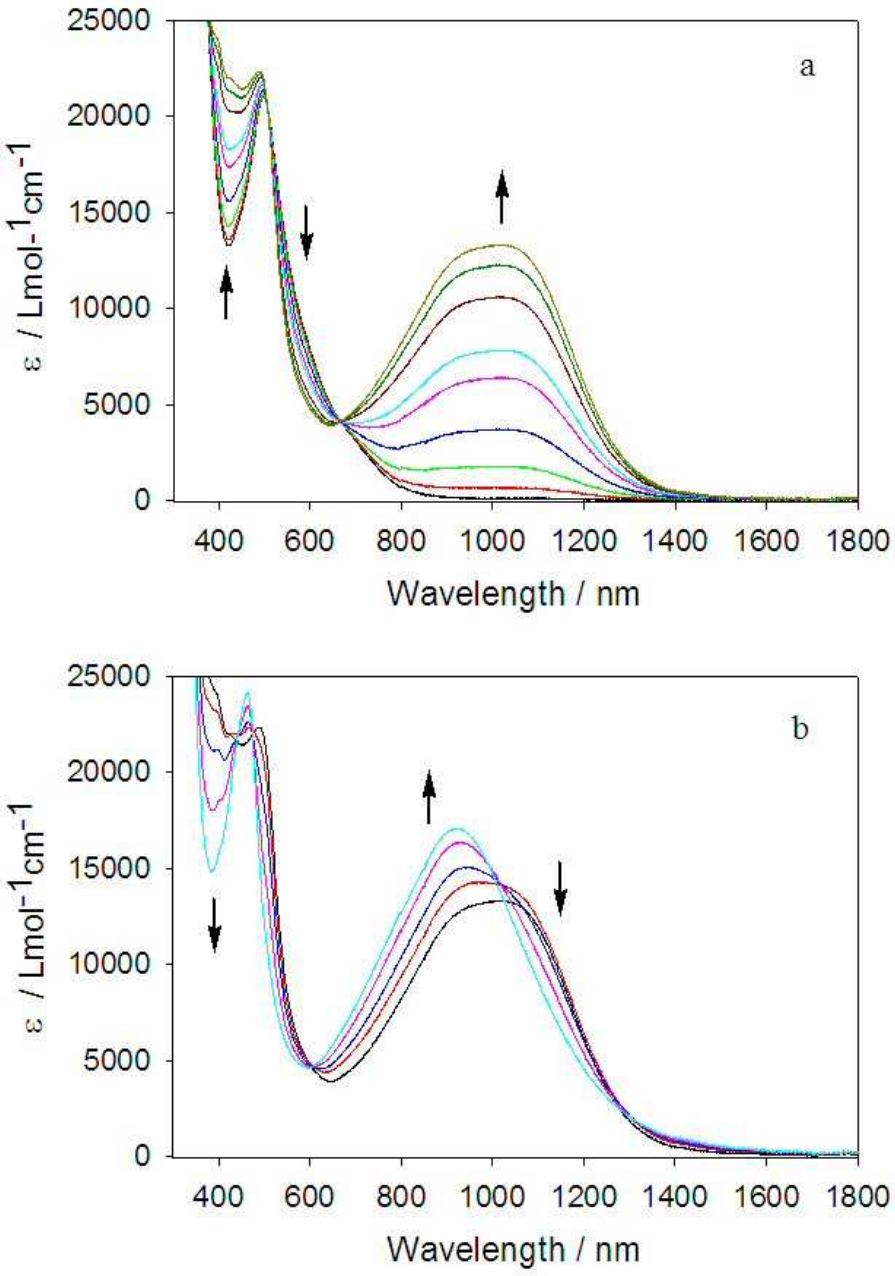

Figure S9. Spectroelectrochemistry of $[\{Ru(ttpy)(bpy)\}_2(\mu\text{-}Me_2dicyd)][PF_6]_2$ in DMF, 0.1 M TBAH a) oxidation to 3+ cation b) oxidation to 4+ cation.

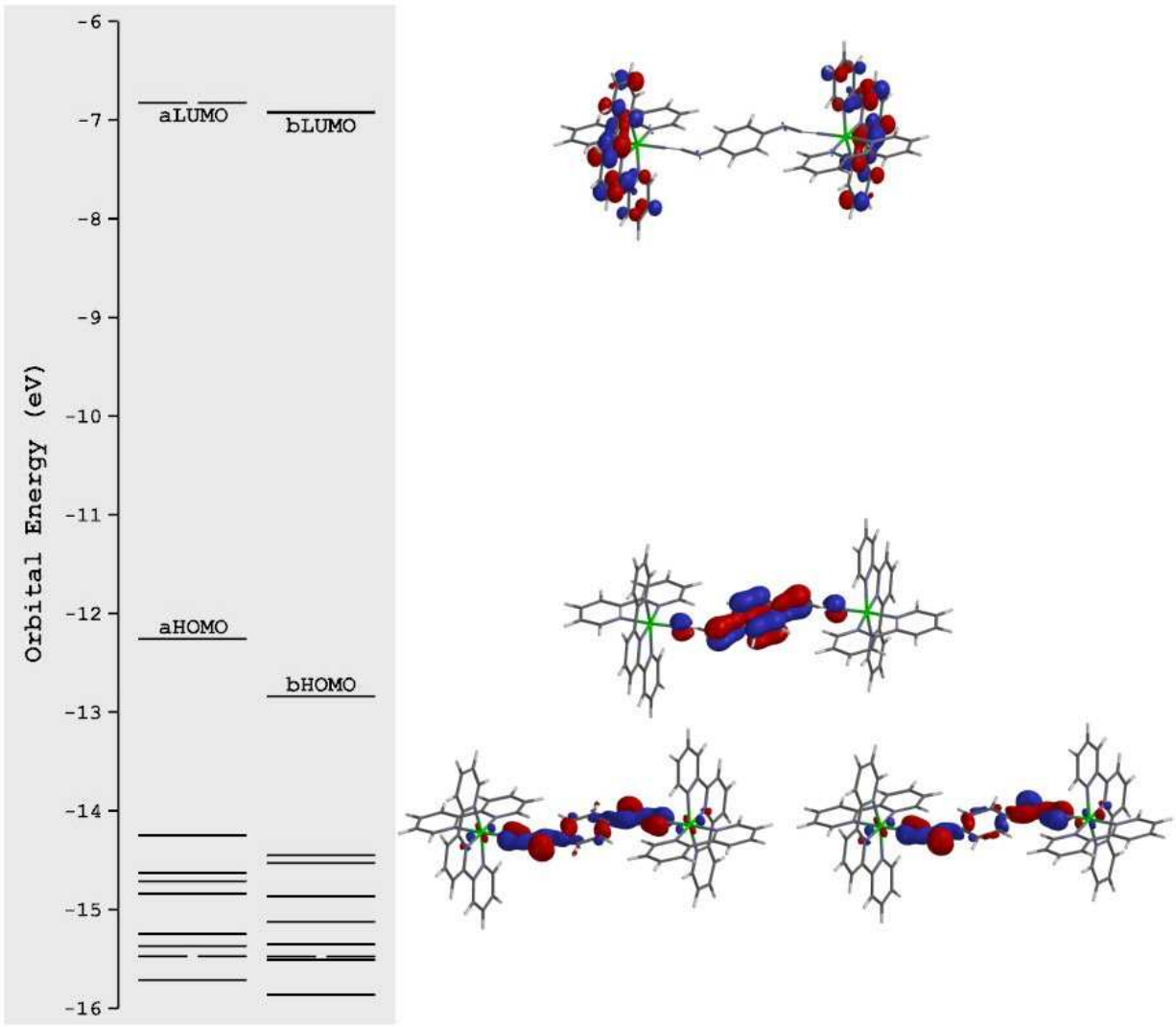

Figure S10. Left side: the gas phase semi-empirical calculation (PM3) of the orbital energies of [{Ru(terpyridine)(bpy)}$_2$(μ-dicyd)]$^{3+}$, **2**$^{+}$. Right side, beta wavefunctions from the top LUMO, HOMO and the two nearly degenerate HOMO(-1) and HOMO(-2).

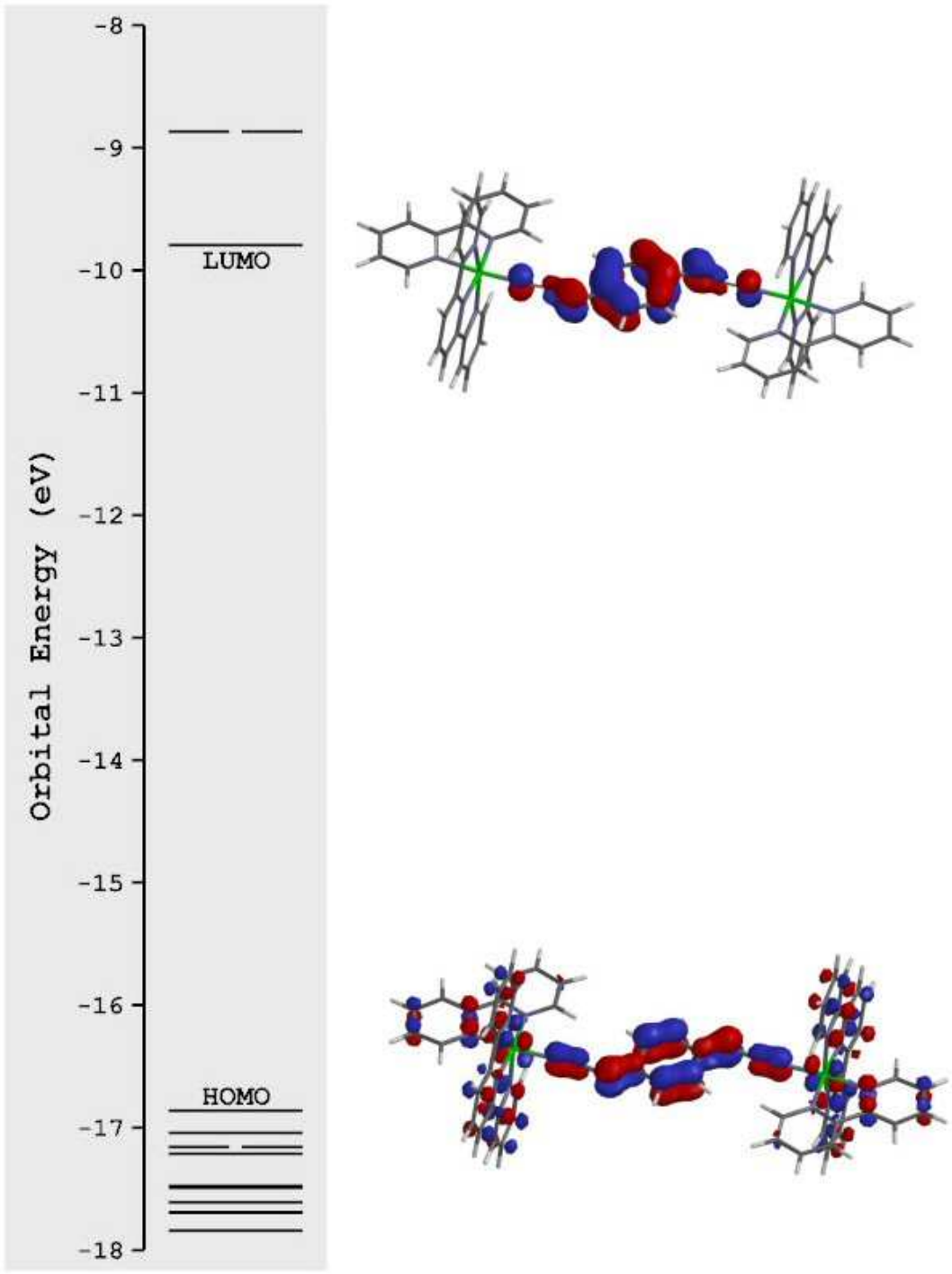

Figure S11. Left side: the gas phase semi-empirical calculation of the orbital energies of $[\{Ru(terpyridine)(bpy)\}_2(\mu\text{-dicyd})]^{4+}$, $\mathbf{2}^{2+}$. Right side, LUMO and HOMO wavefunctions.

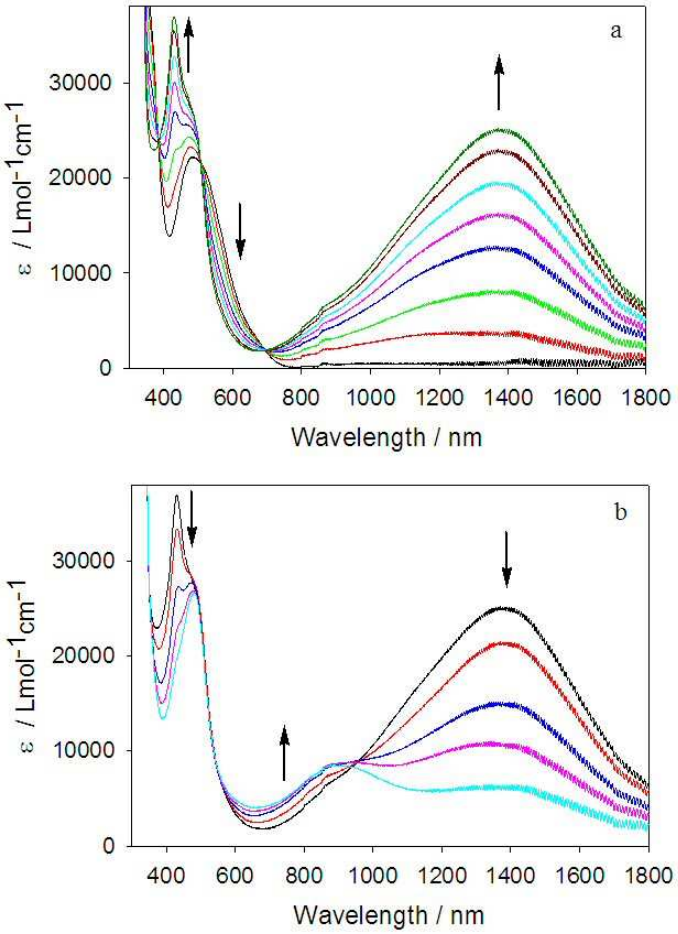

Figure S12. Spectroelectrochemistry of $[\{Ru(ttpy)(bpy)\}_2(\mu\text{-}Cl_4dicyd)][PF_6]_2$ in DMF, 0.1 M TBAH a) oxidation to 3+ cation b) partial oxidation to 4+ cation, loss of isosbestic point indicating irreversibility.

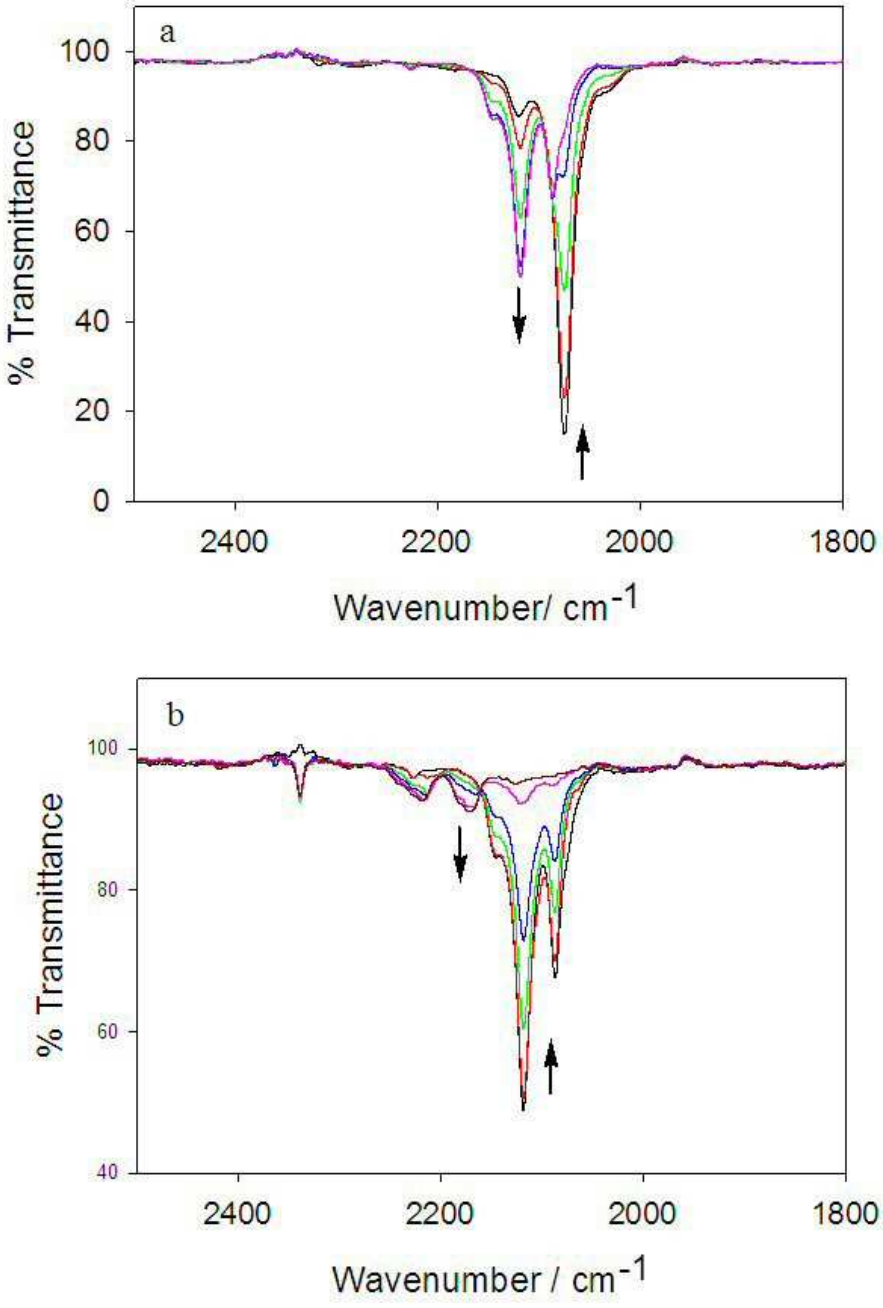

Figure S13. IR spectroelectrochemistry of the tetraphenylarsonium salt of Me_2dicyd^{2-} in DMF, 0.1 M TBAH, a) oxidation to Me_2dicyd^{-} and b) oxidation to Me_2dicyd^{0}

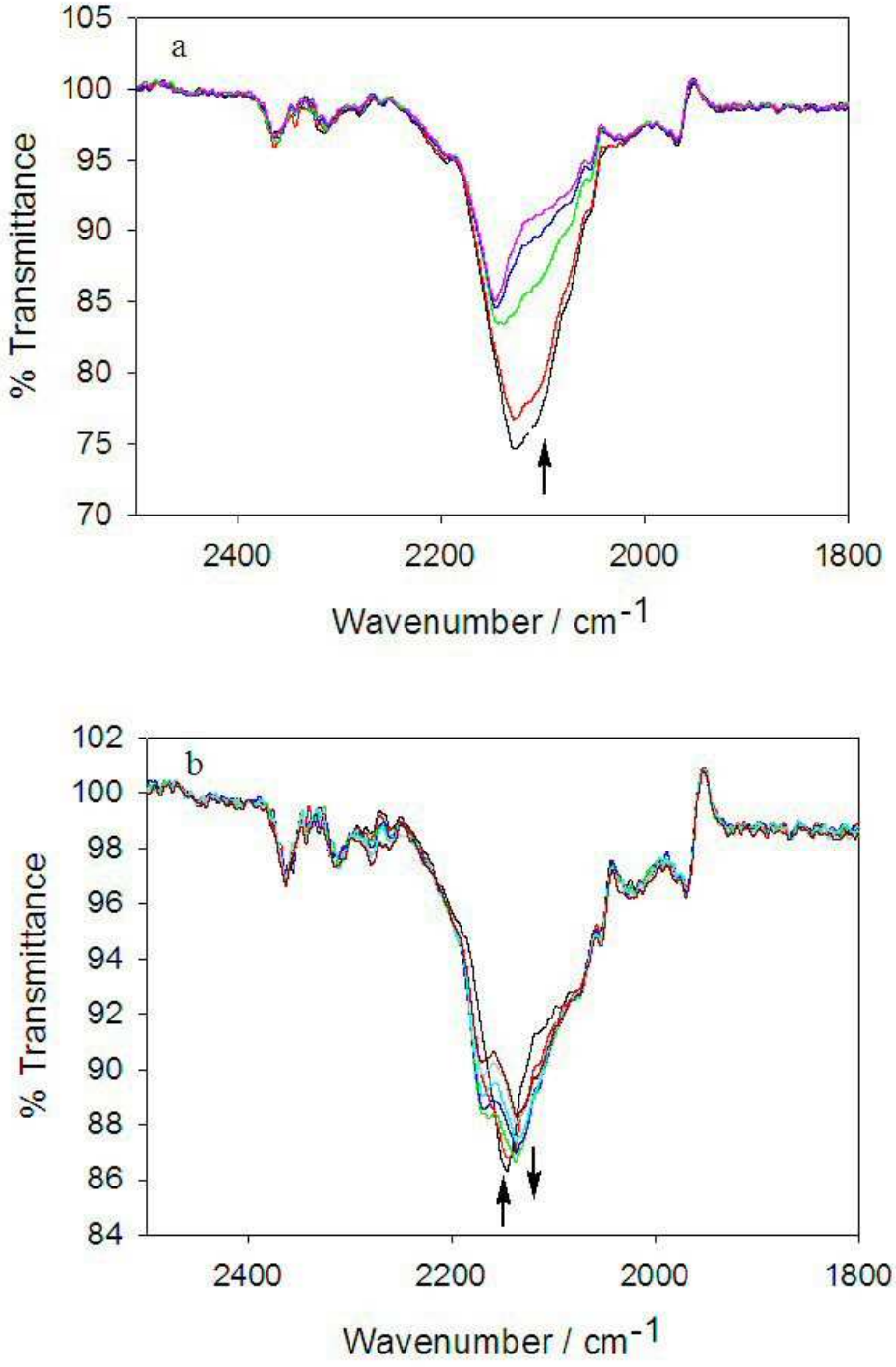

Figure S14. IR spectroelectrochemistry of $[\{Ru(ttpy)(bpy)\}_2(\mu\text{-}Me_2dicyd)][PF_6]_2$ in DMF, 0.1 M TBAH a) oxidation to 3+ cation b) oxidation to 4+ cation.

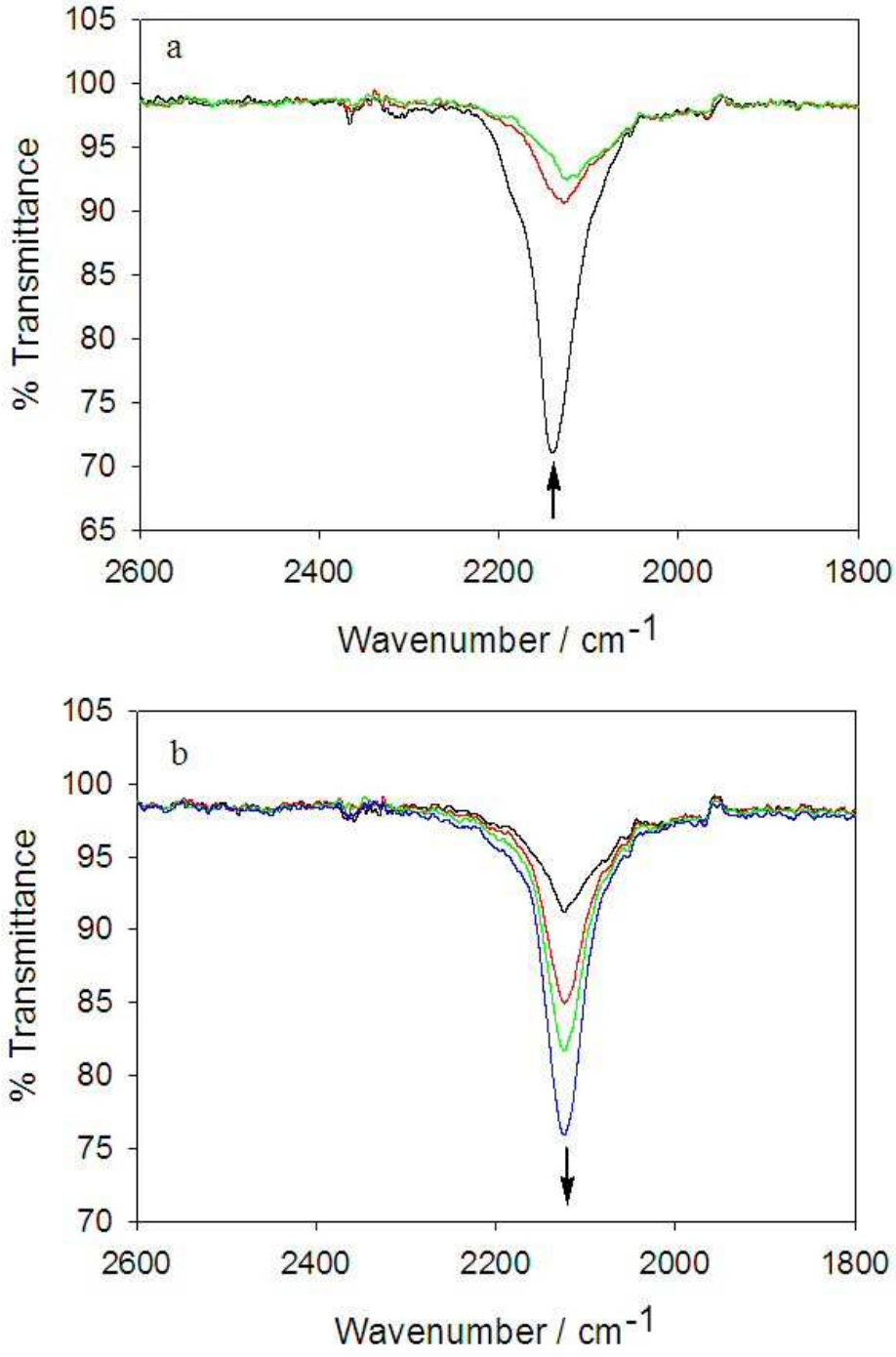

Figure S15. IR spectroelectrochemistry of $[\{Ru(ttpy)(bpy)\}_2(\mu\text{-}Cl_2dicyd)][PF_6]_2$ in DMF, 0.1 M TBAH a) oxidation to 3+ cation b) oxidation to 4+ cation.