A Five-Center Redox System: Molecular Coupling of Two Non-Innocent Imino-*o*-benzoquinonato-Ruthenium Functions through a π Acceptor Bridge

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Supporting Information

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Table S1. DFT G03/PBE0 calculated one-electron energies and compositions of selected highest occupied and lowest unoccupied molecular orbitals of $[Cl(Q)Ru(\mu\text{-tppz})Ru(Q)Cl]^{2+}$ expressed in terms of composing fragments

MO	E (eV)	Prevailing character	Ru	tppz	Q	Cl
Unoccupied	-					
LUMO+4	-6.49	π* tppz	6	92	1	1
LUMO+3	-7.36	π* tppz + Ru	14	67	18	0
LUMO+2	-7.38	π* tppz + Ru	20	69	9	2
LUMO+1	-7.69	π* Q + Ru	17	6	76	1
LUMO	-7.87	π* Q + π* tppz	6	37	55	1
Occupied						
HOMO	-10.03	Ru + Cl	55	11	9	24
HOMO-1	-10.34	Ru + Q + Cl	39	5	37	19
HOMO-2	-10.36	Ru + Q + Cl	38	5	37	20
HOMO-3	-10.60	Cl + Ru	26	18	7	48
HOMO-4	-10.85	Ru + Q	48	14	48	0
HOMO-5	-10.96	Ru + Q	41	9	47	4
HOMO-6	-11.04	Q	12	4	53	31
HOMO-7	-11.09	Q	21	6	44	29

Table S2. Selected G03/PBE0/CPCM calculated lowest allowed TD-DFT singlet transitions for **2^{2+}**.

		calc.		exp.
state	main character (in %)	transition energy[a]	oscill. strength	$\lambda_{max}/\varepsilon$ [b]
^{1}A	42(HOMO-2→LUMO); 43 (HOMO-1→LUMO+1)	1.51(817)	0.018	684 (28750)
^{1}A	75 (HOMO→LUMO+3)	1.98 (625)	0.025	
^{1}A	70 (HOMO→LUMO+2)	2.08 (595)	0.434	
^{1}A	88 ((HOMO-2→LUMO+2)	2.19 (565)	0.209	
^{1}A	mixed	2.36 (523)	0.211	489 (sh)
^{1}A	66 (HOMO-4→LUMO)	2.41 (514)	0.156	
^{1}A	75 ((HOMO-5→LUMO+1)	2.81 (441)	0.130	378 (14850)

[a] Transition energies in eV (wavelengths in nm in parentheses).

[b] Absorption maxima in nm, molar extinction coefficients in M^{-1} cm^{-1}.

Figure S1. Representation frontier orbitals of $\mathbf{2}^{2+}$.

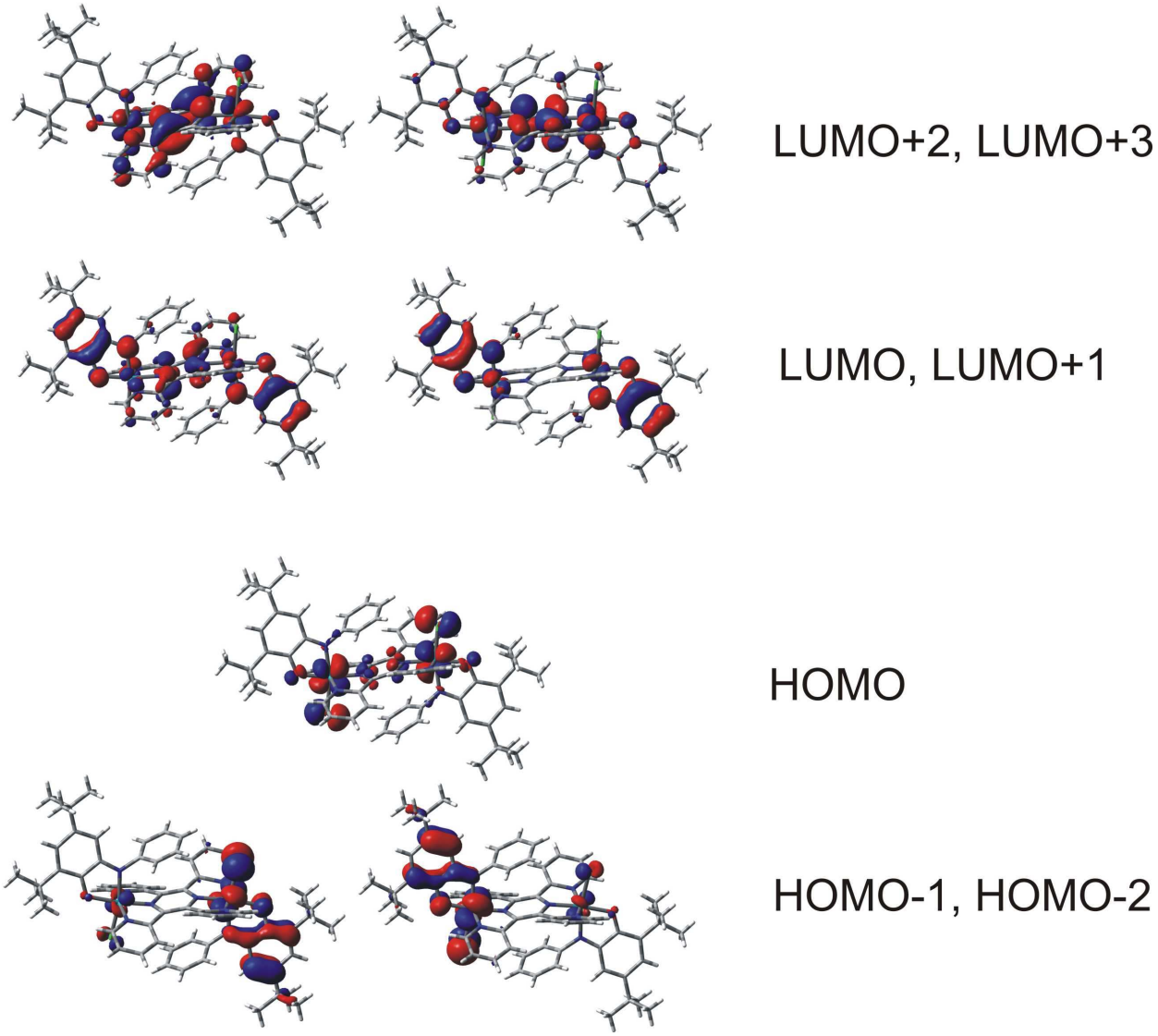
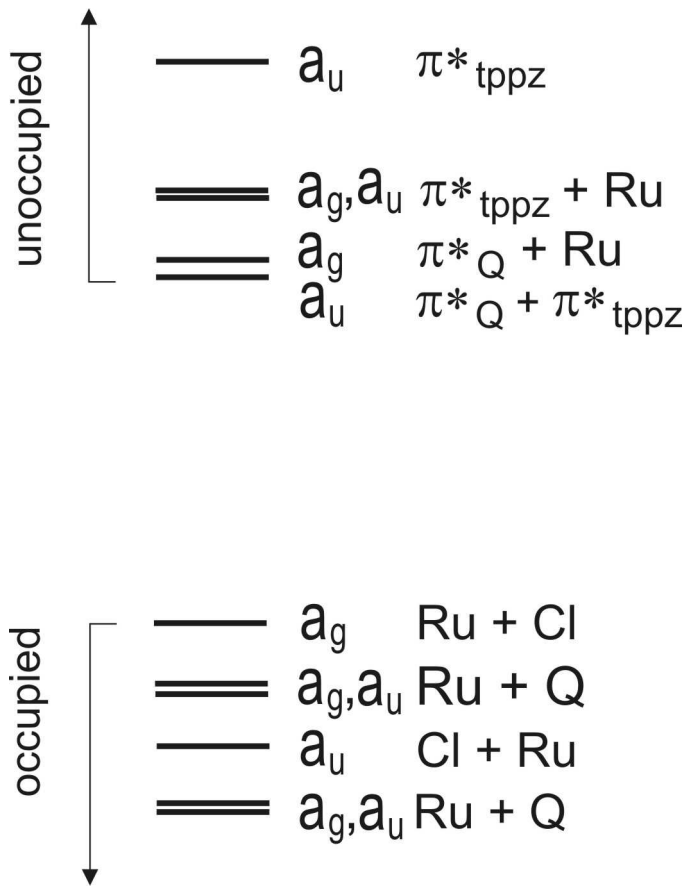
Figure S2. Qualitative DFT calculated MO scheme of $\mathbf{2}^{2+}$. Approximate C_i symmetry is used for the labeling of molecular orbitals.