

Supporting information

Resonance Raman Spectro-Electrochemistry to Illuminate Photo-Induced Molecular Reaction Pathways

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Computational evaluation of the UV-vis-SEC

The main alternations in the absorption spectra upon single reduction (Figure 2B) are associated with IL and MLCT transitions. The electrochemically generated electron residing within the LUMO of the non-reduced complex is photo-excited in case of the energetically low-lying IL transitions (D₇, D₁₃, D₁₄, and partially D₂₂) between 756 (1.64 eV) and 488 nm (2.54 nm). The doublet transitions at higher energies, i.e., between 463 (2.68 eV) and 345 nm (3.60 eV), are mainly of MLCT nature (D₂₅, D₃₅ and D₅₇), while brighter IL $\pi_{\text{tpy}} \rightarrow \pi_{\text{tpy}}^*$ transitions, e.g., state D₆₃ and D₈₀, are found at even higher energies (Table S1). In summary and according to the calculations, the long wavelength absorption feature (> 700 nm) as well as the new absorption band centered at around 630 nm of the single-reduced form are dominated by $\pi_{\text{tpy}}^* \rightarrow \pi_{\text{tpy}}^*$ IL transitions, i.e., D₇ at 756 nm and D₁₃ and D₁₄ at 568 and 557 nm, respectively. Additionally, the shoulder observed at around 536 nm in the experimental spectrum (Figure 1B) can be assigned to a superposition of excitations into the states D₂₂ and D₂₅. The state D₂₂ (488 nm) presents a pronounced mixture of IL ($\pi_{\text{tpy}}^* \rightarrow \pi_{\text{tpy}}^*$) and ²MLCT transitions. D₂₅ (463 nm) is of pure MLCT nature, while the charge density is exclusively shifted upon photoexcitation towards the non-reduced terpyridine ligand in [(tbtpy)Ru(tbtpy^{*})]⁺. Finally, the spectral changes at higher excitation energy around 414 nm can be mainly associated to the population of the D₃₅ (405 nm) and D₅₇ (345 nm) states of mixed MLCT/IL character.

In the following, the observed spectral changes are discussed with respect to both possible scenarios. Considering the formation of the energetically slightly favored doubly reduced triplet species the experimentally observed changes at around 800 nm can be related to the excitation into the doubly degenerated ³IL ($\pi_{\text{terpy}}^* \rightarrow \pi_{\text{terpy}}^*$) states, T₉, and T₁₀, at 758 and 779 nm (Figure 2D). The IL and MLCT states T₁₅ and T₁₆ (584 and 581 nm) may be assigned to the broad absorption band of the experimental spectrum at around 516 nm. Finally, the spectral variations upon double reduction centered at 444 nm can be attributed to the most intense absorption band at 478 nm in the theoretical spectrum, which stems from a superposition of three MLCT states, namely T₃₂, T₃₃, and T₃₅.

Alternatively, the doubly reduced singlet species is considered, where the low-lying $\pi_{\text{tpy}}^* \rightarrow \pi_{\text{tpy}}^*$ IL state, S₇ at 726 nm, is found at a slightly higher excitation energy than the analogous ³IL states T₉ and T₁₀ of the triplet species. Excitation into this S₇ may be associated to the spectral changes in the NIR region, while the variations observed between 470 and 650 nm can be attributed to a superposition of several medium bright singlet excited states (S₁₁, S₁₃, S₁₄, S₁₆, S₁₈, and S₂₀), which are mainly of MLCT character (see Table S1 of SI). The rising absorption feature at 426 nm can be correlated to the superposition of a bright IL/LMCT (S₂₅) and a bright IL state (S₂₆) at 396 and 390 nm, respectively.

Table S1: Calculated bright electronic excited states for the non-reduced (singlet), singly (doublet), and doubly reduced (singlet and triplet) species of [(tbterpy)₂Ru]²⁺ with the main transitions, excitation energies E^e and wavelengths λ , oscillator strengths f , and the eigen values of $\langle s^2 \rangle$.

Non-reduced singlet (S=0)						
State	Transition	Weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
S ₁	d _{yz} (153) $\rightarrow$ π^*_{tpy} (154) (MLCT)	79	2.55	486	0.019	0.000
	d _{yz} (153) $\rightarrow$ π^*_{tpy} (155) (MLCT)	19				
S ₂	d _{yz} (153) $\rightarrow$ π^*_{tpy} (155) (MLCT)	79	2.55	486	0.019	0.000
	d _{yz} (153) $\rightarrow$ π^*_{tpy} (154) (MLCT)	19				
S ₅	d _{yz} (153) $\rightarrow$ π^*_{tpy} (156) (MLCT)	31	2.76	449	0.050	0.000
	d _{xz} (152) $\rightarrow$ π^*_{tpy} (155) (MLCT)	21				
	d _{xy} (151) $\rightarrow$ π^*_{tpy} (154) (MLCT)	19				
	d _{xz} (152) $\rightarrow$ π^*_{tpy} (154) (MLCT)	14				
	d _{xy} (151) $\rightarrow$ π^*_{tpy} (155) (MLCT)	14				
S ₇	d _{yz} (153) $\rightarrow$ π^*_{tpy} (156) (MLCT)	54	2.89	429	0.171	0.000
	d _{xz} (152) $\rightarrow$ π^*_{tpy} (156) (MLCT)	9				
	d _{xy} (151) $\rightarrow$ π^*_{tpy} (154) (MLCT)	8				
S ₈	d _{xz} (152) $\rightarrow$ π^*_{tpy} (156) (MLCT)	69	2.90	428	0.029	0.000
	d _{xy} (151) $\rightarrow$ π^*_{tpy} (156) (MLCT)	27				
S ₉	d _{xy} (151) $\rightarrow$ π^*_{tpy} (156) (MLCT)	65	2.90	428	0.049	0.000
	d _{xz} (152) $\rightarrow$ π^*_{tpy} (156) (MLCT)	19				
	d _{yz} (153) $\rightarrow$ π^*_{tpy} (156) (MLCT)	11				
S ₁₀	d _{xz} (152) $\rightarrow$ π^*_{tpy} (157) (MLCT)	96	2.92	424	0.025	0.000
S ₁₁	d _{xy} (151) $\rightarrow$ π^*_{tpy} (157) (MLCT)	94	2.92	424	0.035	0.000
S ₂₇	d _{yz} (150) $\rightarrow$ π^*_{tpy} (154) (IL)	75	4.09	303	0.275	0.000
	d _{yz} (153) $\rightarrow$ π^*_{tpy} (160) (MLCT)	11				
S ₂₈	π_{tpy} (150) $\rightarrow$ π^*_{tpy} (155) (IL)	76	4.09	303	0.280	0.000
	d _{yz} (153) $\rightarrow$ π^*_{tpy} (159) (MLCT)	11				
Singly reduced doublet (S=1/2)						
State	Transition	Weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
D ₇	π^*_{tpy} (154 α) $\rightarrow$ π^*_{tpy} (161 α) (IL)	74	1.64	756	0.021	0.782
	π^*_{tpy} (154 α) $\rightarrow$ π^*_{tpy} (160 α) (IL)	21				
D ₁₃	π^*_{tpy} (154 α) $\rightarrow$ π^*_{tpy} (164 α) (IL)	92	2.18	568	0.059	0.788
D ₁₄	π^*_{tpy} (154 α) $\rightarrow$ π^*_{tpy} (155 α) (IL)	58	2.22	557	0.016	0.813
	π^*_{tpy} (153 β) $\rightarrow$ π^*_{tpy} (154 β) (MLCT)	29				
D ₂₂	π^*_{tpy} (154 α) $\rightarrow$ π^*_{tpy} (156 α) (IL)	53	2.54	488	0.062	0.768
	d _{xz} (151 β) $\rightarrow$ π^*_{tpy} (155 β) (MLCT)	43				
D ₂₅	d _{yz} (153 α) $\rightarrow$ π^*_{tpy} (157 α) (MLCT)	23	2.68	463	0.061	0.876
	d _{yz} (153 β) $\rightarrow$ π^*_{tpy} (156 β) (MLCT)	17				
	d _{xy} (152 β) $\rightarrow$ π^*_{tpy} (156 β) (MLCT)	14				
	d _{yz} (153 β) $\rightarrow$ π^*_{tpy} (157 β) (MLCT)	11				
	d _{xz} (152 α) $\rightarrow$ π^*_{tpy} (155 α) (MLCT)	7				
	d _{xy} (151 α) $\rightarrow$ π^*_{tpy} (156 α) (MLCT)	7				
D ₃₅	d _{xy} (152 β) $\rightarrow$ π^*_{tpy} (157 β) (MLCT)	40	3.06	405	0.059	0.906
	π^*_{tpy} (154 α) $\rightarrow$ π^*_{tpy} (171 α) (IL)	30				
	d _{yz} (153 α) $\rightarrow$ π^*_{tpy} (157 α) (MLCT)	8				
D ₅₇	d _{xz} (151 β) $\rightarrow$ π^*_{tpy} (159 β) (MLCT)	39	3.60	345	0.036	0.795
	d _{xz} (152 α) $\rightarrow$ π^*_{tpy} (158 α) (MLCT)	38				

	$d_{xz}(152\alpha) \rightarrow \pi^*_{\text{tpy}}(159\alpha)$ (MLCT)	13				
D ₆₃	$\pi^*_{\text{tpy}}(150\beta) \rightarrow \pi^*_{\text{tpy}}(157\beta)$ (IL)	33	3.71	334	0.141	0.948
	$\pi^*_{\text{tpy}}(150\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (IL)	25				
	$d_{yz}(153\beta) \rightarrow \pi^*_{\text{tpy}}(160\beta)$ (MLCT)	10				
D ₈₀	$\pi^*_{\text{tpy}}(149\beta) \rightarrow \pi^*_{\text{tpy}}(154\beta)$ (IL)	46	4.13	300	0.452	0.775
	$\pi^*_{\text{tpy}}(149\alpha) \rightarrow \pi^*_{\text{tpy}}(155\alpha)$ (IL)	44				
Doubly reduced singlet (S=0)						
State	Transition	Weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
S ₇	$\pi^*_{\text{tpy}}(154) \rightarrow \pi^*_{\text{tpy}}(161)$ (IL)	92	1.71	726	0.023	0.000
S ₁₁	$\pi^*_{\text{tpy}}(154) \rightarrow \pi^*_{\text{tpy}}(164)$ (IL)	91	2.24	554	0.036	0.000
S ₁₃	$d_{xy}(152) \rightarrow \pi^*_{\text{tpy}}(156)$ (MLCT)	85	2.36	526	0.039	0.000
S ₁₄	$d_{yz}(153) \rightarrow \pi^*_{\text{tpy}}(155)$ (MLCT)	87	2.46	504	0.028	0.000
S ₁₆	$d_{xy}(152) \rightarrow \pi^*_{\text{tpy}}(155)$ (MLCT)	78	2.51	494	0.021	0.000
	$d_{yz}(153) \rightarrow \pi^*_{\text{tpy}}(157)$ (MLCT)	16				
S ₁₈	$d_{yz}(151) \rightarrow \pi^*_{\text{tpy}}(157)$ (MLCT)	45	2.57	483	0.034	0.000
	$\pi^*_{\text{tpy}}(154) \rightarrow \pi^*_{\text{tpy}}(166)$ (IL)	22				
	$d_{yz}(151) \rightarrow \pi^*_{\text{tpy}}(156)$ (MLCT)	12				
S ₂₀	$d_{yz}(151) \rightarrow \pi^*_{\text{tpy}}(155)$ (MLCT)	60	2.61	475	0.115	0.000
	$d_{xy}(152) \rightarrow \pi^*_{\text{tpy}}(157)$ (MLCT)	24				
S ₂₅	$\pi^*_{\text{tpy}}(154) \rightarrow \pi^*_{\text{tpy}}(169)$ (IL)	51	3.13	396	0.199	0.000
	$\pi^*_{\text{tpy}}(154) \rightarrow d_z(171)$ (LMCT)	34				
S ₂₆	$\pi^*_{\text{tpy}}(154) \rightarrow \pi^*_{\text{tpy}}(170)$ (IL)	88	3.18	390	0.144	0.000
Doubly reduced triplet (S=1)						
State	Transition	Weight / %	E^e / eV	λ / nm	f	$\langle s^2 \rangle$
T ₉	$\pi^*_{\text{tpy}}(154\alpha) \rightarrow \pi^*_{\text{tpy}}(160\alpha)$ (IL)	51	1.58	785	0.010	2.048
	$\pi^*_{\text{tpy}}(155\alpha) \rightarrow \pi^*_{\text{tpy}}(161\alpha)$ (IL)	31				
	$\pi^*_{\text{tpy}}(155\alpha) \rightarrow \pi^*_{\text{tpy}}(159\alpha)$ (IL)	15				
T ₁₀	$\pi^*_{\text{tpy}}(155\alpha) \rightarrow \pi^*_{\text{tpy}}(160\alpha)$ (IL)	46	1.59	779	0.016	2.044
	$\pi^*_{\text{tpy}}(154\alpha) \rightarrow \pi^*_{\text{tpy}}(159\alpha)$ (IL)	27				
	$\pi^*_{\text{tpy}}(154\alpha) \rightarrow \pi^*_{\text{tpy}}(161\alpha)$ (IL)	24				
T ₁₅	$\pi^*_{\text{tpy}}(155\alpha) \rightarrow \pi^*_{\text{tpy}}(163\alpha)$ (IL)	43	2.12	584	0.048	2.138
	$\pi^*_{\text{tpy}}(154\alpha) \rightarrow \pi^*_{\text{tpy}}(164\alpha)$ (IL)	36				
T ₁₆	$d_{xy}(151\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (MLCT)	33	2.13	581	0.042	2.105
	$d_{yz}(153\beta) \rightarrow \pi^*_{\text{tpy}}(157\beta)$ (MLCT)	29				
	$d_{xz}(151\alpha) \rightarrow \pi^*_{\text{tpy}}(157\alpha)$ (MLCT)	19				
T ₃₂	$d_{xz}(151\alpha) \rightarrow \pi^*_{\text{tpy}}(157\alpha)$ (MLCT)	35	2.56	484	0.037	2.105
	$d_{xy}(151\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (MLCT)	15				
	$d_{xy}(151\beta) \rightarrow \pi^*_{\text{tpy}}(154\beta)$ (MLCT)	13				
	$d_{xz}(152\beta) \rightarrow \pi^*_{\text{tpy}}(157\beta)$ (MLCT)	11				
	$d_{xz}(152\beta) \rightarrow \pi^*_{\text{tpy}}(155\beta)$ (MLCT)	9				
T ₃₃	$d_{yz}(153\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (MLCT)	33	2.57	481	0.068	2.236
	$d_{xz}(152\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (MLCT)	15				
	$d_{yz}(153\beta) \rightarrow \pi^*_{\text{tpy}}(154\beta)$ (MLCT)	13				
	$d_{xy}(152\alpha) \rightarrow \pi^*_{\text{tpy}}(157\alpha)$ (MLCT)	7				
	$d_{yz}(153\alpha) \rightarrow \pi^*_{\text{tpy}}(156\alpha)$ (MLCT)	6				
T ₃₅	$d_{xz}(152\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (MLCT)	56	2.61	476	0.083	2.211
	$d_{yz}(153\beta) \rightarrow \pi^*_{\text{tpy}}(156\beta)$ (MLCT)	21				
	$d_{xy}(151\beta) \rightarrow \pi^*_{\text{tpy}}(157\beta)$ (MLCT)	7				

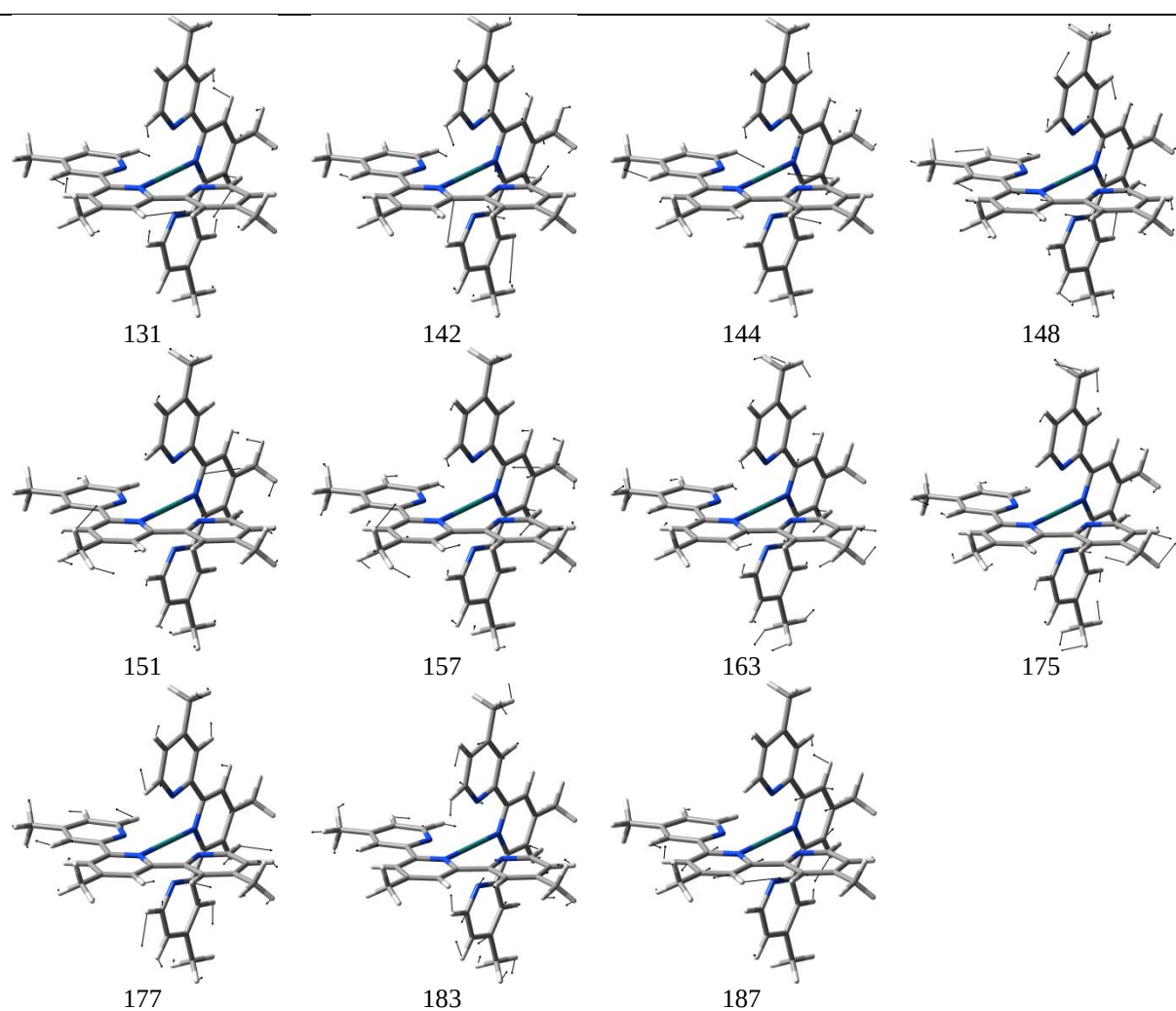


Figure S1: Resonance Raman active vibrational modes of non-reduced singlet species ($S=0$, $\lambda_{\text{exc}} = 514 \text{ nm}$).

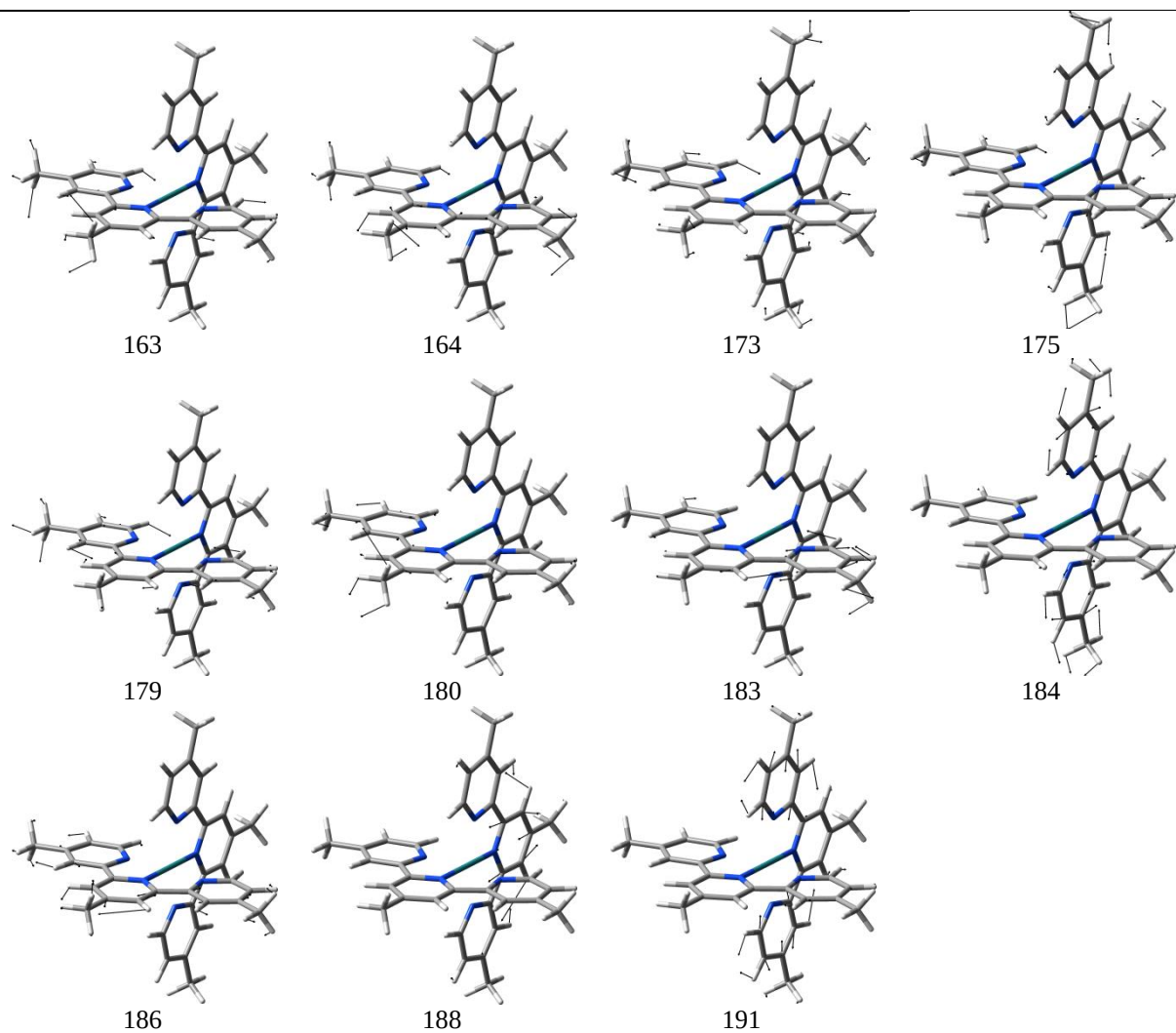


Figure S2: Resonance Raman active vibrational modes of singly reduced doublet species ($S=1/2$, $\lambda_{\text{exc}} = 514 \text{ nm}$).

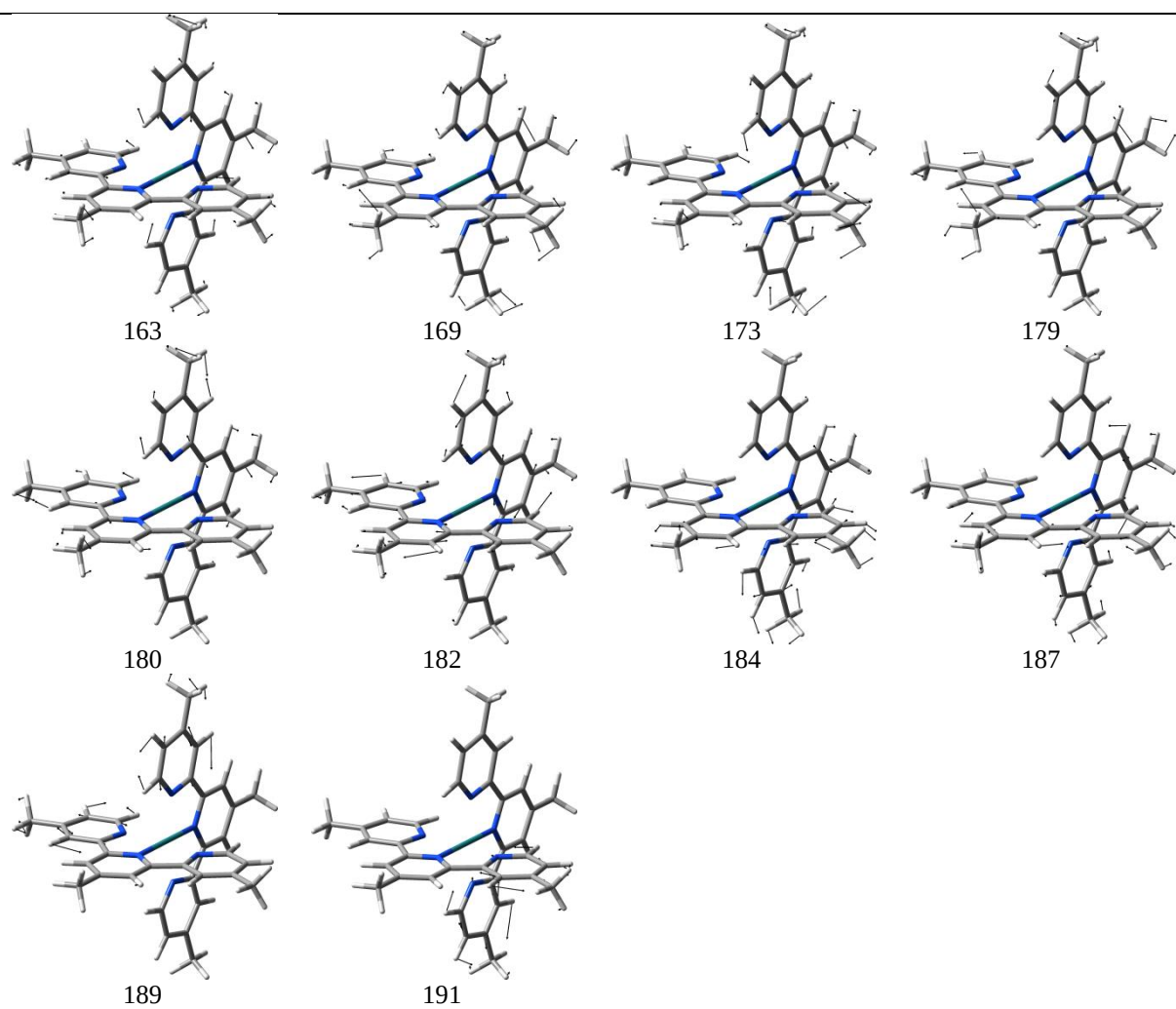


Figure S3: Resonance Raman active vibrational modes of doubly reduced triplet species ($S=1$, $\lambda_{\text{exc}} = 514\text{nm}$).

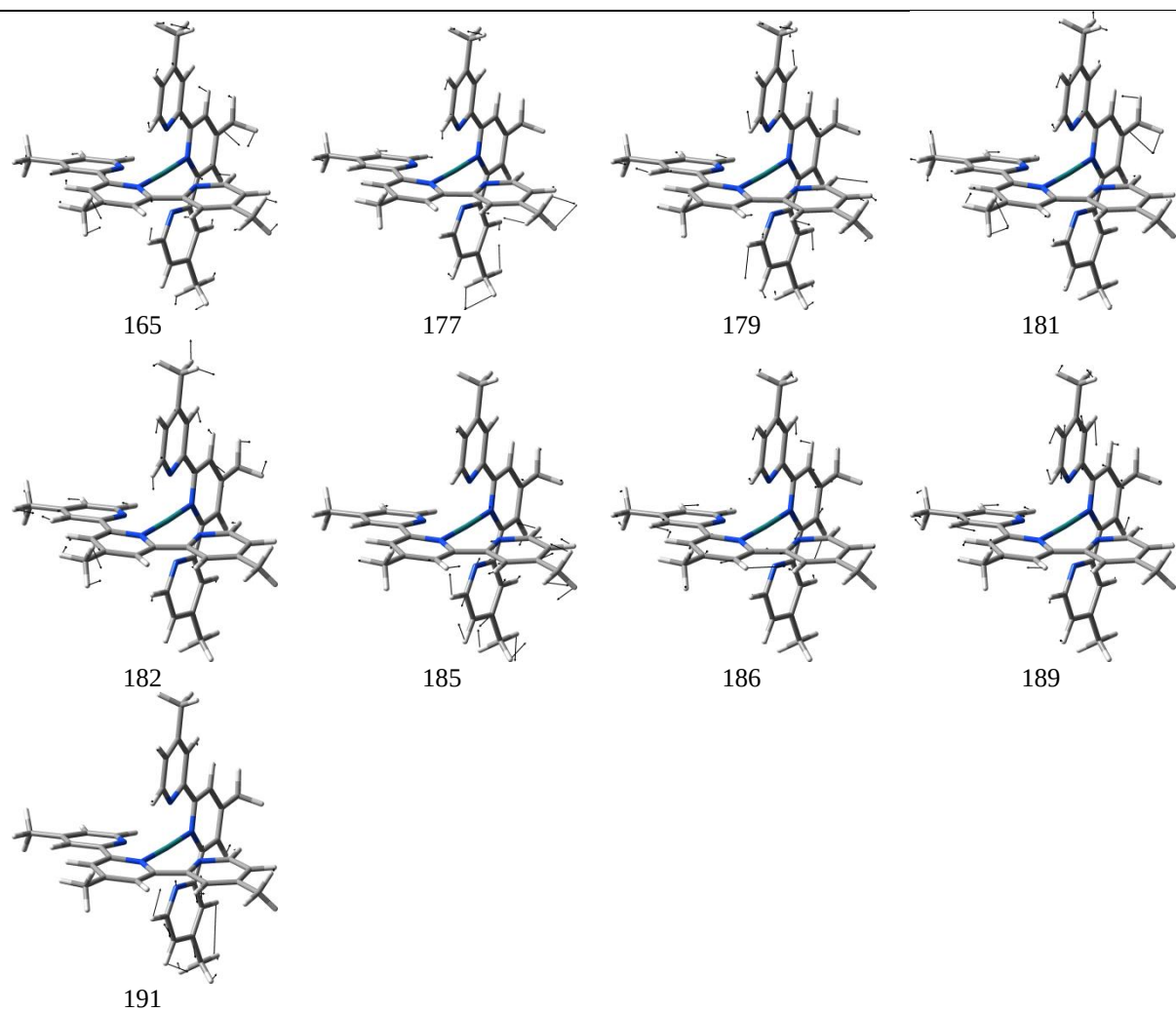


Figure S4: Resonance Raman active vibrational modes of doubly reduced singlet species ($S=0$, $\lambda_{\text{exc}} = 514\text{nm}$).

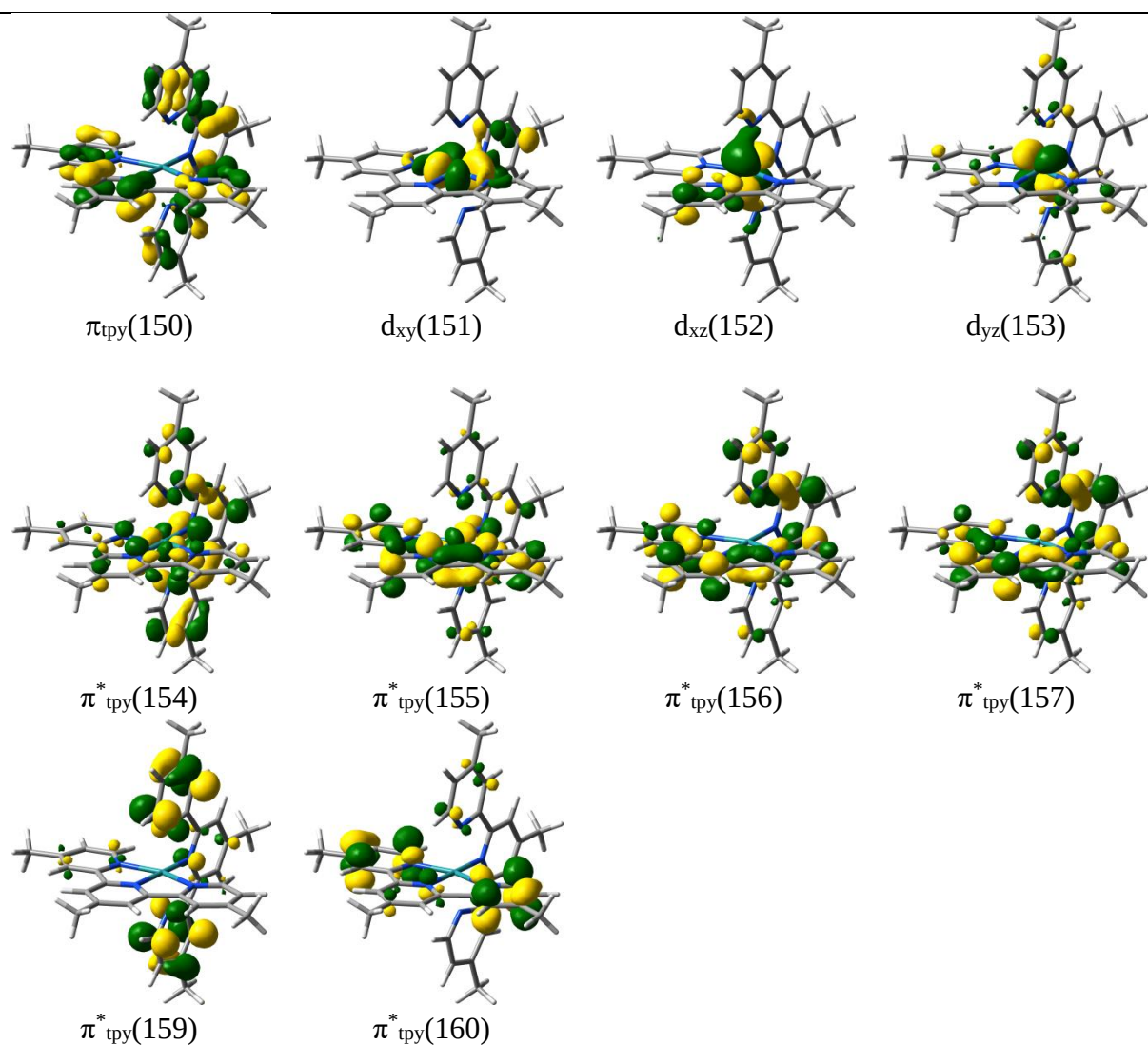
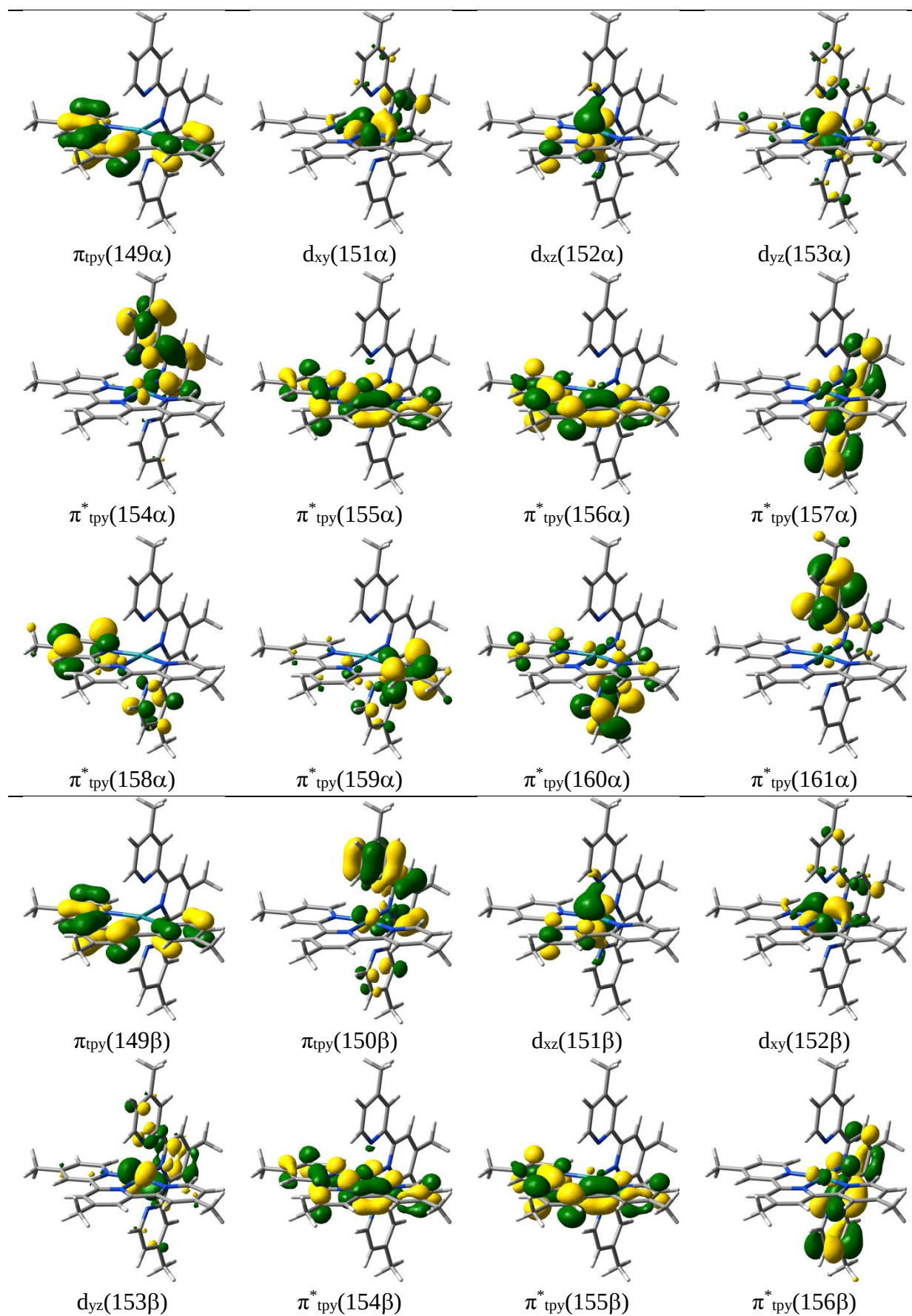


Figure S5: Molecular orbitals involved in the main transitions of the bright excited states calculated at the B3LYP/6-31G(d) level of theory for the non-reduced ($S=0$) ruthenium complex.



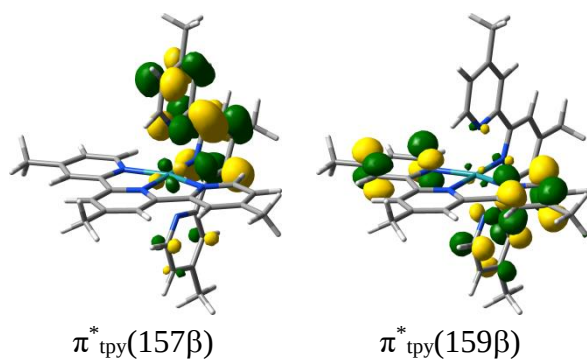


Figure S6: Molecular orbitals involved in the main transitions of the bright excited states calculated at the B3LYP/6-31G(d) level of theory for the singly reduced ($S=1/2$) ruthenium complex.

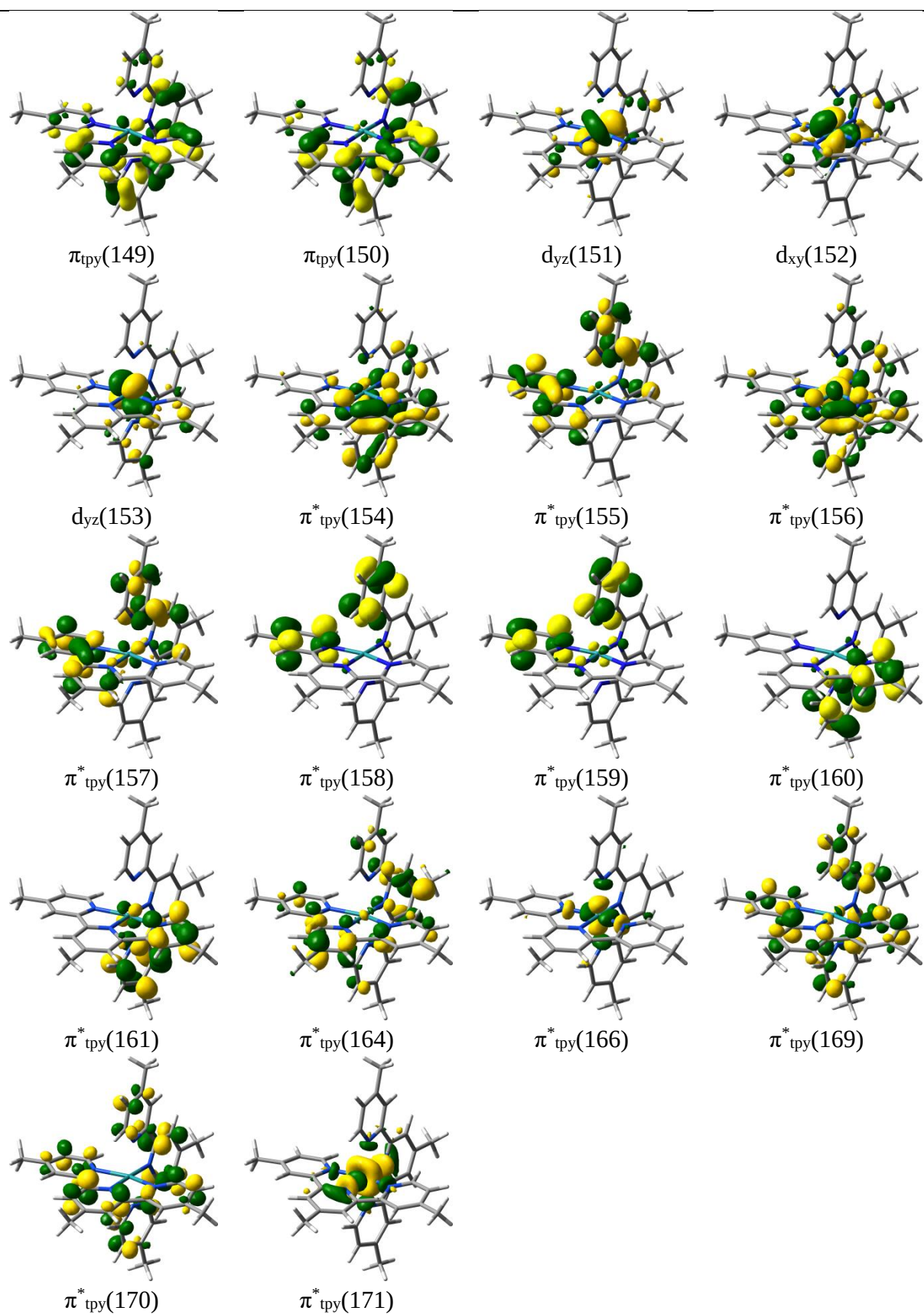


Figure S7: Molecular orbitals involved in the main transitions of the bright excited states calculated at the B3LYP/6-31G(d) level of theory for the doubly reduced (singlet multiplicity, $S=0$) ruthenium complex.

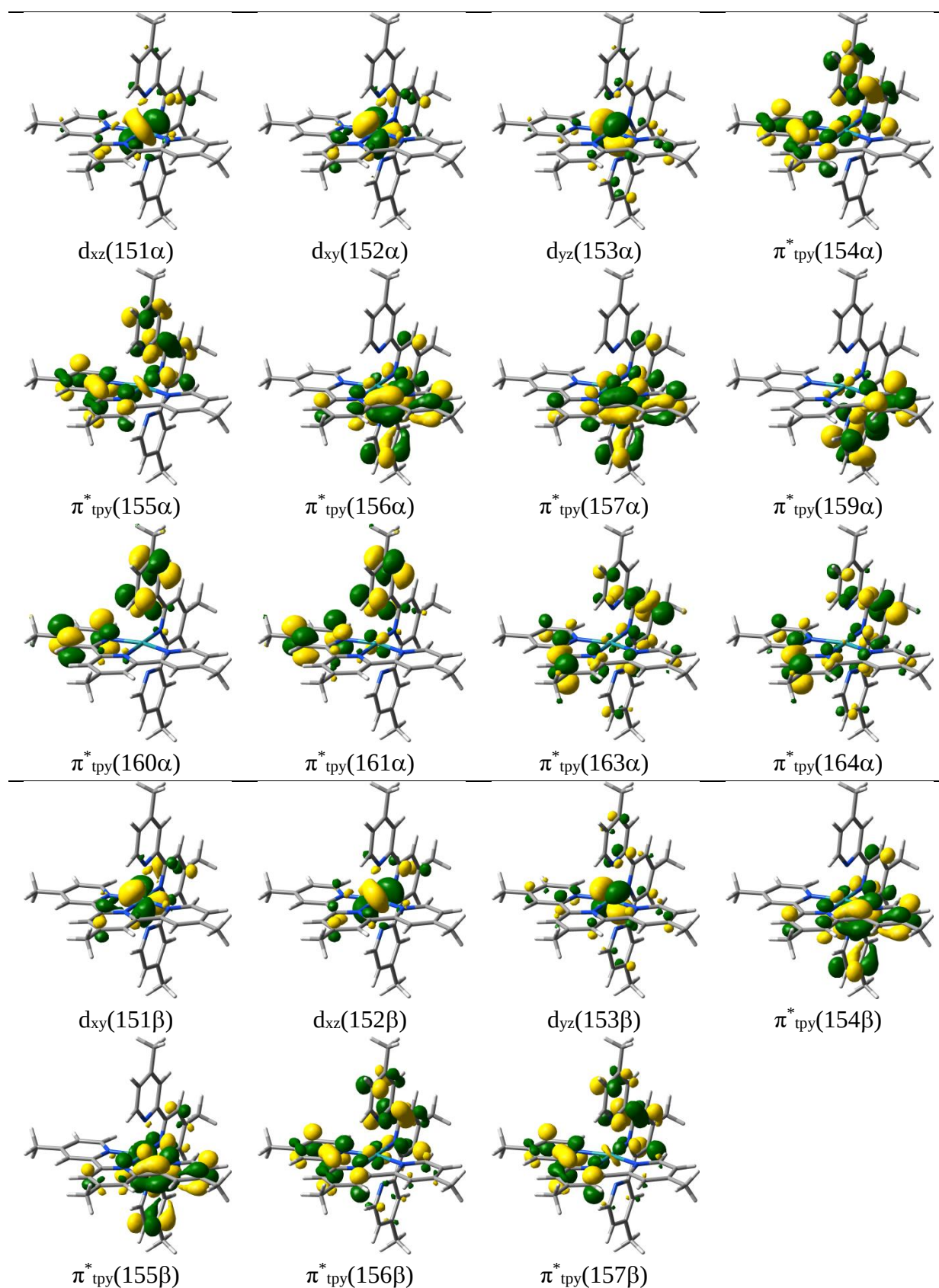
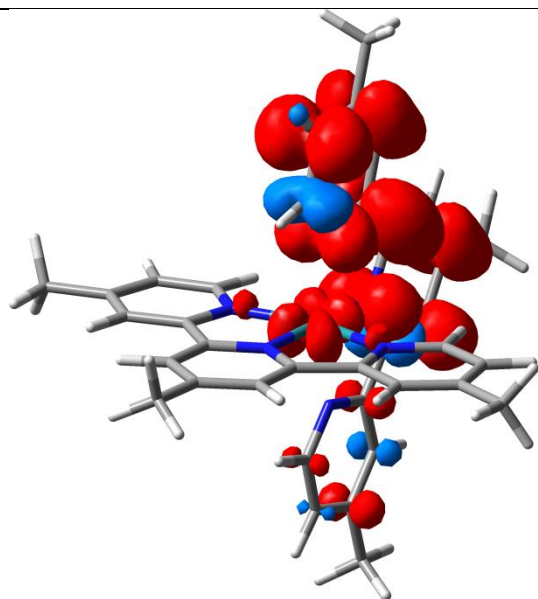
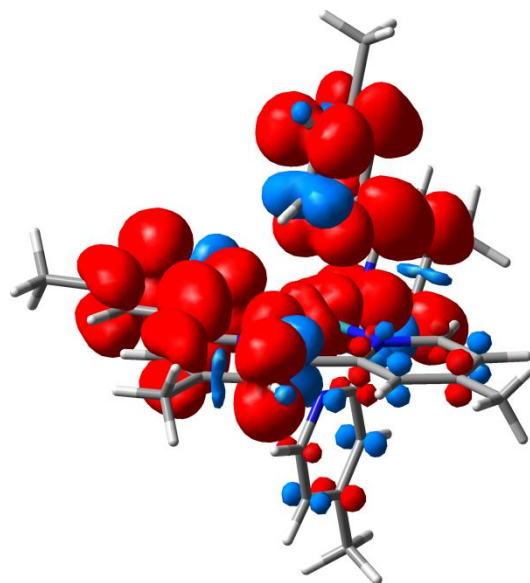


Figure S8: Molecular orbitals involved in the main transitions of the bright excited states calculated at the B3LYP/6-31G(d) level of theory for the doubly reduced (triplet multiplicity, $S=1$) ruthenium complex.



Singly reduced doublet



Doubly reduced triplet

Figure S9: Spin densities of the singly (doublet multiplicity, $S=1/2$) and doubly reduced (triplet multiplicity, $S=1$) ruthenium complex.