

X-Ray Transient Absorption Structural Characterization of the $^3\text{MLCT}$ Triplet Excited State of *cis*-[Ru(bpy)₂(py)₂]²⁺

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Supporting Information

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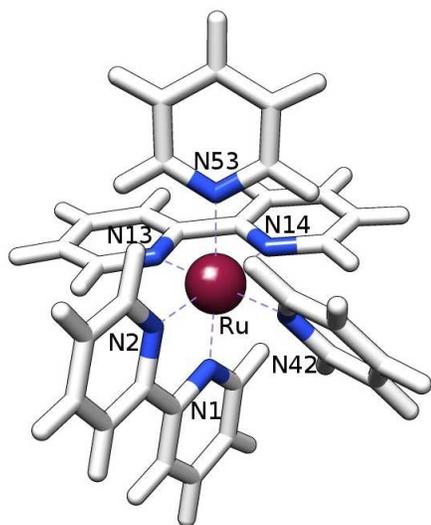
A – Computational Data

A1. Computational details

All calculations were performed with the Gaussian 09 (G09) program,¹ employing the DFT method. For *cis*-[Ru(bpy)₂(py)₂]²⁺, the singlet ground state (GS) geometry and the triplet geometries corresponding to a ³MLCT and ³MC state (lowest-lying) were fully optimized with the B3LYP^{2, 3} and PBE0^{4, 5} functionals at either the LanL2DZ/6-31+G** or LanL2DZ/6-311G** level.^{6, 7} Triplet geometries were obtained using the unrestricted Kohn-Sham formalism (UKS).⁸ In the case of the photoproduct *cis*-[Ru(bpy)₂(py)(H₂O)]²⁺, only the singlet ground state geometry was optimized with the same functionals and basis sets. All optimizations were performed including the solvent effect (CPCM method)⁹⁻¹¹ with water or dichloromethane as solvent. The ³MC state geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ computed at the B3LYP/LanL2DZ/6-31+G** level could not be optimized with the CPCM solvent model. Only for this case we performed the geometry optimization in the gas phase. The nature of all stationary points was confirmed by normal-mode analysis. A set of other six functionals (TPSSH,^{12,13} M06,¹³ mPW1PBE, mPW1LYP,¹⁴ m062X,¹³ HSEh1PBE¹⁵) was tested as well for the optimization of the ³MLCT and ³MC geometries of *cis*-[Ru(bpy)₂(py)₂]²⁺.

Fifty singlet-singlet electronic transitions were calculated by TDDFT,^{16, 17} employing the ground state structures optimized with the B3LYP and PBE0 functionals together with the LanL2DZ/6-31+G** and LanL2DZ/6-311G** basis sets. The same methods were adopted to calculate four singlet-triplet electronic transitions from the ³MLCT and ³MC state geometries, while sixteen triplet-triplet transitions were calculated from the same triplet geometries by TDDFT/PBE0/LanL2DZ/6-311G** to aid the assignment of the transient absorption experiment. Solvent effects were considered using the CPCM method and water as solvent. The program GaussSum 1.05¹⁸ was adopted to simulate the electronic spectra of the ruthenium complex and to visualize the singlet excited state transitions as electron density difference maps (EDDMs). Computational results are summarized in the tables and graphics below.

Molecular graphics images were produced using the UCSF Chimera package from the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco (supported by NIH P41 RR001081).¹⁹



Scheme A1. Atom-numbering scheme for complex *cis*-[Ru(bpy)₂(py)₂]²⁺.

A2. Geometry optimizations

Table A1. Calculated bond lengths for the singlet ground state (GS) and triplet ³MLCT and ³MC states of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water. Solvent effects were included using the CPCM method. The LanL2DZ ECP was employed for the Ru atom in all calculations.

Bond lengths – GS						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
B3LYP/ 6-31+G**	2.10259	2.12146	2.10257	2.12145	2.17384	2.17382
B3LYP/ 6-311G**	2.10464	2.12287	2.10464	2.12286	2.17518	2.17517
PBE0/ 6-31+G**	2.07556	2.09187	2.07556	2.09186	2.13571	2.13570
PBE0/ 6-311G**	2.07627	2.09209	2.07627	2.09208	2.13559	2.13558
Average	2.08976	2.10707	2.08976	2.10706	2.15508	2.15507
Bond lengths – ³ MLCT						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
B3LYP/ 6-31+G**	2.03755	2.08232	2.09092	2.14513	2.17467	2.21023
B3LYP/ 6-311G**	2.04618	2.08438	2.09443	2.14586	2.17739	2.20936
PBE0/ 6-31+G**	2.06639	2.11384	2.02104	2.05892	2.17129	2.13942
PBE0/ 6-311G**	2.02713	2.06077	2.06827	2.11325	2.14076	2.16950
TPSSh/ 6-311G**	2.03809	2.06718	2.07935	2.12008	2.14749	2.17310
M06/ 6-311G**	2.05237	2.07297	2.08410	2.13411	2.15277	2.18739
mPW1PBE/ 6-311G**	2.02693	2.06111	2.06844	2.11364	2.14152	2.17041
mPW1LYP/ 6-311G**	2.04627	2.08651	2.09498	2.14803	2.17784	2.21079
m062X/ 6-311G**	2.03792	2.07337	2.08753	2.14808	2.15756	2.19219
HSEh1PBE/ 6-311G**	2.03016	2.06476	2.07205	2.11763	2.14345	2.17192
Average	2.04090	2.07672	2.07611	2.12447	2.15847	2.18343
Bond lengths – ³ MC						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
B3LYP/ 6-31+G**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
B3LYP/ 6-311G**	2.39654	2.19274	2.11545	2.11600	2.16988	3.05937
PBE0/ 6-31+G**	2.37337	2.16741	2.09550	2.09018	2.13560	2.76960
PBE0/ 6-311G**	2.36813	2.16202	2.09710	2.09354	2.14162	2.80235
TPSSh/ 6-311G**	2.35651	2.16621	2.09708	2.09377	2.15467	2.86803

M06/ 6-311G**	2.36324	2.17640	2.11450	2.11181	2.13707	2.79295
mPW1PBE/ 6-311G**	2.36738	2.15829	2.09456	2.09189	2.14640	2.88357
mPW1LYP/ 6-311G**	2.39910	2.19344	2.12421	2.11789	2.16665	3.16614
m062X/ 6-311G**	2.41366	2.22839	2.13711	2.13724	2.16186	2.78585
HSEh1PBE/ 6-311G**	2.37321	2.16988	2.10093	2.09740	2.14301	2.76736
Average	2.37902	2.17942	2.10849	2.10552	2.15075	2.87725

n.d.= not determined. All our attempts to optimize the ³MC geometry at the B3LYP/6-31+G** with the CPCM solvent model were not successful.

Table A2. Calculated bond lengths for the singlet ground state (GS) of *cis*-[Ru(bpy)₂(py)(H₂O)]²⁺ (PHP) in water. Solvent effects were included using the CPCM method. The LanL2DZ ECP was employed for the Ru atom in all calculations.

Bond lengths – GS						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–O53(H ₂ O)
B3LYP/ 6-31+G**	2.05793	2.10717	2.09799	2.11866	2.16651	2.23388
B3LYP/ 6-311G**	2.06486	2.09824	2.10413	2.12030	2.16455	2.23856
PBE0/ 6-31+G**	2.03071	2.08070	2.07180	2.08992	2.12946	2.20497
PBE0/ 6-311G**	2.03721	2.07069	2.07660	2.09148	2.12792	2.20723
Average	2.04768	2.08920	2.08763	2.10509	2.14711	2.22116

Table A3. Calculated bond lengths for the triplet ³MLCT and ³MC states of *cis*-[Ru(bpy)₂(py)₂]²⁺ in dichloromethane. Solvent effects were included using the CPCM method. The LanL2DZ ECP was employed for the Ru atom in all calculations.

Bond lengths – ³ MLCT						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
PBE0/ 6-311G**	2.02522	2.05937	2.06919	2.11496	2.14086	2.17135
TPSSH/ 6-311G**	2.03689	2.06618	2.08011	2.12138	2.14739	2.17404
M06/ 6-311G**	2.05241	2.07227	2.08514	2.13664	2.15281	2.19068
m062X/ 6-311G**	2.03586	2.07152	2.08860	2.15082	2.15768	2.19478
Average	2.03760	2.06734	2.08076	2.13095	2.14968	2.18271
Bond lengths – ³ MC						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
PBE0/ 6-311G**	2.36858	2.16506	2.09731	2.09274	2.13807	2.77434
TPSSH/ 6-311G**	2.35850	2.16755	2.10271	2.09323	2.14729	2.80889
M06/ 6-311G**	2.36446	2.17650	2.11528	2.11160	2.13665	2.77980
m062X/ 6-311G**	2.41584	2.22738	2.13854	2.13683	2.15991	2.76488
Average	2.37685	2.18412	2.11346	2.10860	2.14548	2.78198

A3. TDDFT electronic transitions

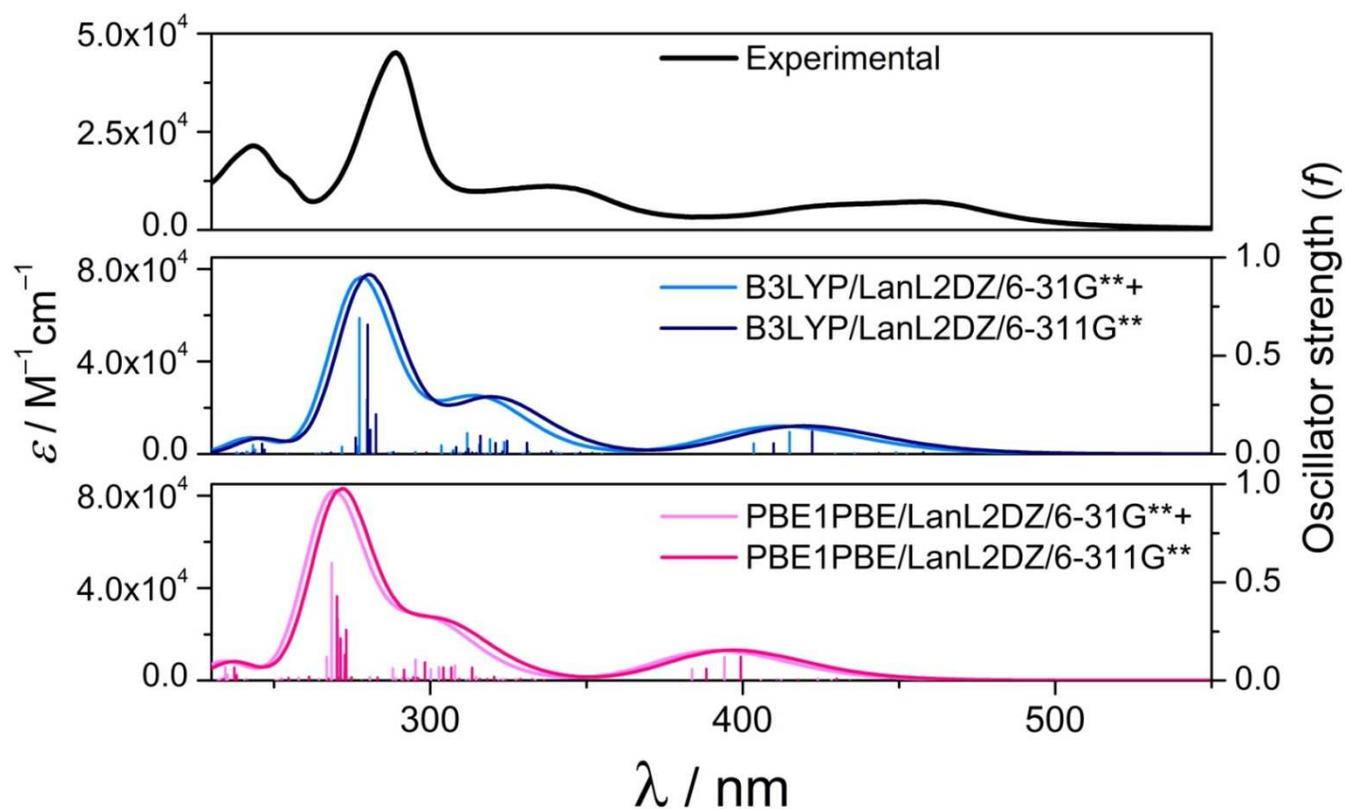
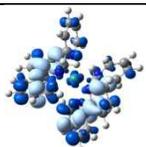
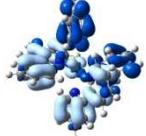


Figure A1. Experimental (black line) and calculated (colored lines) absorption spectra of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water. The singlet excited transitions are shown as vertical bars with heights equal to the extinction coefficients. The theoretical curve was obtained using the program GAUSSSUM 1.05.

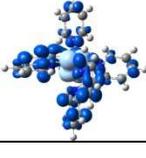
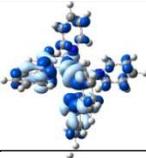
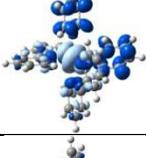
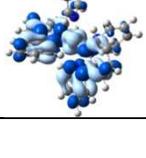
Table A4. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the B3LYP/LanL2DZ/6-31+G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

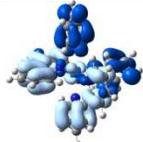
Tr.	E _{calc} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
5	2.9879 (414.95)	0.1122	H-2→L+1 (76%) H-1→LUMO (18%)	MLCT (Ru→bpy)	
6	3.0727 (403.51)	0.0528	H-2→LUMO (53%) H-1→L+1 (30%)	MLCT (Ru→bpy)	
12	3.7418 (331.35)	0.0134	H-2→L+2 (11%) H-1→L+3 (65%) HOMO→L+4 (15%)	MLCT (Ru→py)	
15	3.8309 (323.64)	0.0608	H-2→L+2 (83%)	MLCT (Ru→bpy)	
17	3.8849 (319.14)	0.0748	H-2→L+3 (10%) H-1→L+4 (31%) HOMO→L+5 (11%) HOMO→L+7 (26%)	MLCT (Ru→py/bpy)	
19	3.9270 (315.72)	0.0471	H-2→L+4 (77%) H-1→L+7 (7%)	MLCT (Ru→py)	
20	3.9766 (311.78)	0.1056	HOMO→L+6 (78%)	MLCT (Ru→bpy)	
23	4.0346 (307.3)	0.0189	H-1→L+5 (69%) H-1→L+7 (13%)	MLCT (Ru→bpy)	
26	4.0842 (303.57)	0.0437	H-2→L+5 (54%) H-2→L+7 (37%)	MLCT (Ru→bpy)	
27	4.2003 (295.18)	0.0103	H-1→L+6 (14%) H-1→L+10 (18%) HOMO→L+8 (27%) HOMO→L+11 (23%)	MLCT (Ru→py/bpy)	
35	4.4320 (279.75)	0.2771	H-4→LUMO (35%) H-3→L+1 (34%)	LC (bpy) + MLCT (Ru→bpy)	
36	4.4710 (277.31)	0.6917	H-4→L+1 (42%) H-3→LUMO (29%) H-2→L+6 (9%)	MLCT (Ru→bpy)	
37	4.4763 (276.98)	0.0398	H-2→L+8 (63%) H-2→L+11 (13%)	MLCT (Ru→py)	
38	4.5631 (271.71)	0.0373	HOMO→L+9 (96%)	MLCT (Ru→py)	

45	5.0822 (243.96)	0.0219	H-3→L+2 (78%)	LC (bpy)	
46	5.0963 (243.28)	0.0462	H-4→L+2 (60%) H-3→L+3 (26%)	LC/IL (bpy→py)	
48	5.1397 (241.23)	0.0111	H-4→L+3 (55%) H-3→L+4 (14%)	IL (bpy→py)	

f = oscillator strength

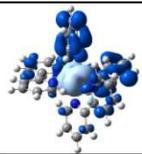
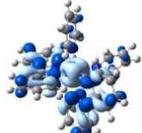
Table A5. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the B3LYP/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

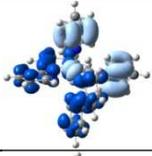
Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
5	2.9368 (422.18)	0.1136	H-2→LUMO (77%) H-1→L+1 (18%)	MLCT (Ru→bpy)	
6	3.0250 (409.86)	0.0536	H-2→L+1 (55%) H-1→LUMO (29%) HOMO→L+1 (11%)	MLCT (Ru→bpy)	
12	3.6604 (338.71)	0.0142	H-2→L+2 (10%) H-1→L+3 (74%) HOMO→L+4 (9%)	MLCT (Ru→py)	
15	3.7464 (330.95)	0.057	H-2→L+2 (82%)	MLCT (Ru→bpy)	
17	3.8198 (324.59)	0.0671	H-1→L+4 (35%) HOMO→L+5 (29%) HOMO→L+7 (16%)	MLCT (Ru→py/bpy)	
18	3.8370 (323.13)	0.013	H-2→L+3 (12%) HOMO→L+5 (57%) HOMO→L+7 (21%)	MLCT (Ru→bpy/py)	
19	3.8637 (320.90)	0.0565	H-2→L+4 (80%)	MLCT (Ru→py)	
20	3.9231 (316.04)	0.0924	H-1→L+7 (-11%) HOMO→L+6 (74%)	MLCT (Ru→bpy)	
23	3.9713 (312.20)	0.0268	H-1→L+5 (39%) H-1→L+7 (34%), H-2→L+10 (7%) HOMO→L+6 (9%)	MLCT (Ru→bpy)	
25	4.0216 (308.29)	0.0348	H-2→L+5 (39%) H-2→L+7 (53%)	MLCT (Ru→bpy)	
35	4.3867 (282.64)	0.2016	H-4→L+1 (26%) H-3→LUMO (25%) H-2→L+8 (15%)	LC (bpy) + MC	
36	4.4152 (280.81)	0.1228	H-4→L+1 (16%) H-3→LUMO (12%) H-2→L+8 (42%) H-2→L+11 (10%)	MLCT (Ru→py)	
37	4.4286 (279.96)	0.6576	H-4→LUMO (42%) H-3→L+1 (28%)	LC (bpy) + MLCT (Ru→bpy)	

38	4.4906 (276.10)	0.0831	HOMO→L+9 (91%)	MLCT (Ru→py)	
45	5.0212 (246.92)	0.0224	H-3→L+2 (79%)	LC (bpy)	
46	5.0370 (246.15)	0.0521	H-4→L+2 (68%) H-3→L+3 (18%)	LC/IL (bpy→py)	
48	5.0972 (243.24)	0.0093	H-4→L+3 (61%) H-3→L+4 (13%)	IL (bpy→py)	

f = oscillator strength

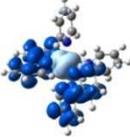
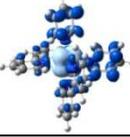
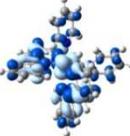
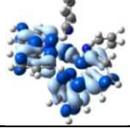
Table A6. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-31+G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

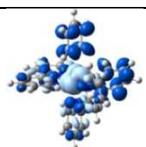
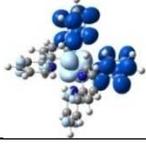
Tr.	E _{calc.} , eV (nm)	f	Composition	Character	EDDMs
5	3.1459 (394.11)	0.1197	H-2→L+1 (73%) H-1→LUMO (19%)	MLCT (Ru→bpy)	
6	3.2309 (383.74)	0.0573	H-2→LUMO (44%) H-1→L+1 (36%) HOMO→LUMO (15%)	MLCT (Ru→bpy)	
12	3.9408 (314.62)	0.0181	H-2→L+2 (12%) H-1→L+3 (73%)	MLCT (Ru→py)	
15	4.0267 (307.90)	0.0754	H-2→L+2 (78%)	MLCT (Ru→bpy)	
17	4.0955 (302.73)	0.0667	H-1→L+4 (57%) HOMO→L+7 (18%)	MLCT (Ru→py)	
19	4.1305 (300.17)	0.0573	H-2→L+4 (75%)	MLCT (Ru→py)	
20	4.1988 (295.28)	0.1047	HOMO→L+6 (77%)	MLCT (Ru→bpy)	
21	4.2313 (293.02)	0.0111	H-1→L+6 (60%) HOMO→L+7 (13%)	MLCT (Ru→bpy)	
24	4.2608 (290.99)	0.0109	H-1→L+5 (67%) H-1→L+7 (14%)	MLCT (Ru→bpy)	
25	4.2894 (289.04)	0.0106	H-2→L+6 (71%)	MLCT (Ru→bpy)	
26	4.3050 (288.00)	0.0611	H-2→L+5 (54%) H-2→L+7 (33%)	MLCT (Ru→bpy)	
27	4.4177 (280.65)	0.0181	H-1→L+6 (13%) H-1→L+11 (14%) HOMO→L+8 (24%) HOMO→L+12 (23%)	MLCT (Ru→py/bpy)	
32	4.5706 (271.27)	0.0525	H-4→L+1 (25%) H-3→LUMO (60%)	LC (bpy) + MC	
33	4.5839 (270.48)	0.3116	H-4→LUMO (28%) H-3→L+1 (32%)	LC (bpy) + MC	
34	4.6188 (268.43)	0.5983	H-4→L+1 (49%) H-3→LUMO (11%) H-2→L+6 (10%)	LC (bpy) + MC	

36	4.6457 (266.88)	0.1201	H-1→L+8 (83%)	MLCT (Ru→py)	
38	4.8081 (257.87)	0.0140	HOMO→L+9 (97%)	MLCT (Ru→py)	
39	4.9105 (252.49)	0.0111	H-5→LUMO (63%) H-2→L+9 (26%)	M(L)LCT (Ru(py)→bpy)	
45	5.2721 (235.17)	0.0301	H-3→L+2 (73%)	LC (bpy)	
46	5.2892 (234.41)	0.0680	H-4→L+2 (67%)	LC (bpy)	

f = oscillator strength

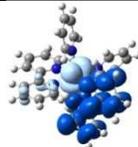
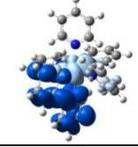
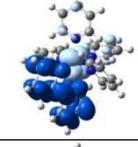
Table A7. Selected TDDFT singlet-singlet transitions and corresponding electron difference density maps (EDDMs) for *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	
5	3.1045 (399.37)	0.1215	H-2→L+1 (73%) H-1→LUMO (19%)	MLCT (Ru→bpy)	
6	3.1929 (388.31)	0.0586	H-2→LUMO (45%) H-1→L+1 (35%) HOMO→LUMO (14%)	MLCT (Ru→bpy)	
12	3.8694 (320.42)	0.0185	H-2→L+2 (12%) H-1→L+3 (76%)	MLCT (Ru→py)	
15	3.9566 (313.36)	0.0650	H-2→L+2 (66%)	MLCT (Ru→bpy)	
17	4.0426 (306.69)	0.0658	H-1→L+4 (54%) HOMO→L+5 (14%) HOMO→L+7 (15%)	MLCT (Ru→py)	
19	4.0759 (304.19)	0.0658	H-2→L+4 (77%)	MLCT (Ru→py)	
20	4.1564 (298.30)	0.0921	H-1→L+7 (10%) HOMO→L+6 (73%)	MLCT (Ru→bpy)	
22	4.1901 (295.90)	0.0131	H-2→L+5 (17%) H-1→L+6 (43%) HOMO→L+7 (13%)	MLCT (Ru→bpy)	
24	4.2087 (294.59)	0.0157	H-1→L+5 (43%) H-1→L+7 (33%)	MLCT (Ru→bpy)	
25	4.2499 (291.73)	0.0102	H-2→L+6 (76%)	MLCT (Ru→bpy)	
26	4.2514 (291.63)	0.0541	H-2→L+5 (44%) H-2→L+7 (43%)	MLCT (Ru→bpy)	
27	4.3794 (283.11)	0.0148	H-1→L+6 (13%) H-1→L+11 (11%) HOMO→L+8 (33%) HOMO→L+12 (18%)	MLCT (Ru→py/bpy)	
29	4.5113 (274.83)	0.0163	H-2→L+8 (15%) H-1→L+11 (24%) HOMO→L+8 (17%)	MLCT (Ru→py/bpy)	
31	4.5399 (273.10)	0.2579	H-3→L+1 (55%) HOMO→L+8 (14%)	LC (bpy) + MLCT (Ru→py)	
32	4.5468 (272.69)	0.1317	H-4→L+1 (14%) H-3→LUMO (71%)	LC (bpy) + MC	
33	4.5478	0.0461	H-4→LUMO (67%)	LC (bpy) + MC	

	(272.63)		H-3→L+1 (18%)		
34	4.5708 (271.26)	0.2152	H-4→L+1 (38%) H-1→L+8 (45%)	MLCT (Ru→py) + LC (bpy)	
35	4.5762 (270.93)	0.0128	H-2→L+8 (18%) HOMO→L+8 (20%)	MLCT (Ru→py/bpy)	
36	4.5899 (270.12)	0.4291	H-4→L+1 (31%) H-1→L+8 (46%)	MLCT (Ru→py) + LC (bpy)	
38	4.7461 (261.24)	0.0192	HOMO→L+9 (97%)	M(L)LCT (Ru(bpy)→py)	
40	4.8687 (254.66)	0.0129	H-5→LUMO (14%) H-2→L+9 (79%)	MLCT (Ru→py)	
45	5.2085 (238.04)	0.0274	H-3→L+2 (74%)	LC (bpy)	
46	5.2255 (237.27)	0.0657	H-4→L+2 (68%)	LC (bpy)	

f = oscillator strength

Table A8. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MLCT geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the B3LYP/LanL2DZ/6-31+G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	2.0146 (615.42)	0	HOMO→LUMO (89%)	M(L)LCT (Ru(bpy)→bpy)	
2	2.2471 (551.75)	0	H-1→LUMO (94%)	M(L)LCT (Ru(py)→bpy)	
3	2.4149 (513.42)	0	H-2→LUMO (95%)	M(L)LCT (Ru(bpy/py)→bpy)	
4	2.5285 (490.35)	0	HOMO→L+1 (88%)	M(L)LCT (Ru(bpy)→bpy)	

f = oscillator strength

Table A9. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MLCT geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the B3LYP/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

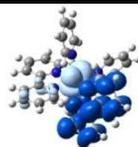
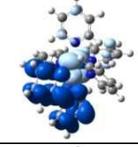
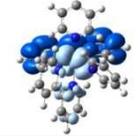
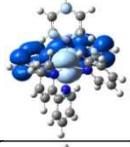
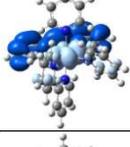
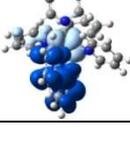
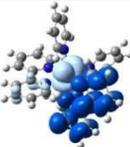
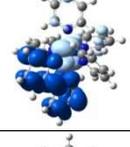
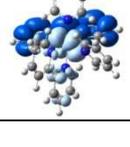
Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	1.9870 (623.98)	0	HOMO→LUMO (91%)	M(L)LCT (Ru(bpy)→bpy)	
2	2.2014 (563.21)	0	H-1→LUMO (94%)	M(L)LCT (Ru(py)→bpy)	
3	2.3640 (524.46)	0	H-2→LUMO (95%)	M(L)LCT (Ru(bpy/py)→bpy)	
4	2.4929 (497.35)	0	HOMO→L+1 (89%)	M(L)LCT (Ru(bpy)→bpy)	

Table A10. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MLCT geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-31+G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	2.0735 (597.94)	0	HOMO→LUMO (81%)	M(L)LCT (Ru(bpy)→bpy)	
2	2.3468 (528.32)	0	H-1→LUMO (86%)	M(L)LCT (Ru(py)→bpy)	
3	2.5599 (484.32)	0	H-2→LUMO (90%)	M(L)LCT (Ru(bpy/py)→bpy)	
4	2.6031 (476.29)	0	HOMO→L+1 (73%)	M(L)LCT (Ru(bpy)→bpy)	

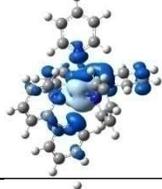
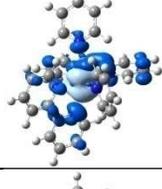
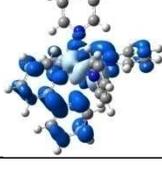
f = oscillator strength

Table A11. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MLCT geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	2.0578 (602.50)	0	HOMO→LUMO (83%)	M(L)LCT (Ru(bpy)→bpy)	
2	2.3125 (536.15)	0	H-1→LUMO (86%)	M(L)LCT (Ru(py)→bpy)	
3	2.5201 (491.97)	0	H-2→LUMO (89%)	M(L)LCT (Ru(bpy/py)→bpy)	
4	2.5820 (480.19)	0	HOMO→L+1 (77%)	M(L)LCT (Ru(bpy)→bpy)	

f = oscillator strength

Table A12. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MC geometry (gas phase) of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the B3LYP/LanL2DZ/6-31+G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	0.4824 (2570.15)	0	HOMO→LUMO (68%) H-1→LUMO (20%) HOMO→L+2 (17%)	MC/MLCT (Ru→bpy)	
2	0.9011 (1375.87)	0	H-2→LUMO (35%) H-1→LUMO (35%)	MC/MLCT (Ru→bpy)	
3	0.9911 (1251.0)	0	H-2→LUMO (41%) H-1→LUMO (24%) H-2→L+2 (11%)	MC/MLCT (Ru→bpy)	
4	2.6234 (472.62)	0	HOMO→L+1 (39%) HOMO→LUMO (18%) HOMO→L+2 (-18%)	MC/MLCT (Ru→bpy)	

f = oscillator strength

Table A13. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MC geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the B3LYP/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	-0.2119 (-5851.46)	0	HOMO→LUMO (108%) HOMO→L+2 (26%) H-1→LUMO (25%)	MC/MLCT (Ru→bpy)	
2	0.6486 (1911.49)	0	H-2→LUMO (45%) H-1→LUMO (39%) H-2→L+2 (10%)	MC/MLCT (Ru→bpy)	
3	0.7973 (1555.01)	0	H-2→LUMO (42%) H-1→LUMO (32%) H-2→L+2 (10%) HOMO→LUMO (10%)	MC/MLCT (Ru→bpy)	
4	2.5522 (485.79)	0	HOMO→L+2 (69%) HOMO→LUMO (17%)	MC/MLCT (Ru→bpy)	

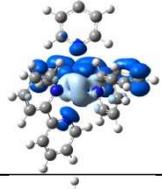
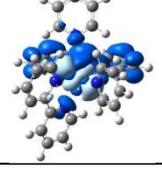
f = oscillator strength

Table A14. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MC geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-31+G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	0.1912 (6485.73)	0	HOMO→L+2 (87%) HOMO→LUMO (78%) H-1→L+2 (13%) H-1→LUMO (12%)	MC/MLCT (Ru→bpy)	
2	0.8477 (1462.53)	0	H-2→L+2 (39%) H-2→LUMO (37%) H-1→L+2 (13%) H-1→LUMO (12%)	MC/MLCT (Ru→bpy)	
3	0.9734 (1273.68)	0	H-1→L+2 (33%) H-1→LUMO (30%) H-2→L+2 (14%) H-2→LUMO (12%)	MC/MLCT (Ru→bpy)	
4	2.6364 (470.27)	0	HOMO→LUMO (38%) HOMO→L+2 (32%)	MC/MLCT (Ru→bpy)	

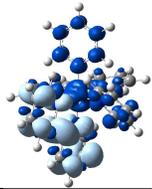
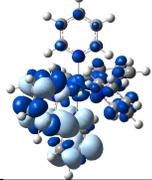
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Table A15. TDDFT singlet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MC geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
1	-0.1589 (-7800.86)	0	HOMO→L+2 (98%) HOMO→LUMO (83%) H-1→L+2 (16%) H-1→LUMO (13%)	MC/MLCT (Ru→bpy)	
2	0.7988 (1552.05)	0	H-2→L+2 (42%) H-2→LUMO (38%) H-1→L+2 (11%) H-1→LUMO (10%)	MC/MLCT (Ru→bpy)	
3	0.928 (1335.98)	0	H-1→L+2 (35%) H-1→LUMO (31%) H-2→L+2 (12%) H-2→LUMO (10%)	MC/MLCT (Ru→bpy)	
4	2.6131 (474.46)	0	HOMO→LUMO (41%) HOMO→L+2 (33%)	MC/MLCT (Ru→bpy)	

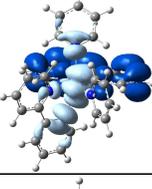
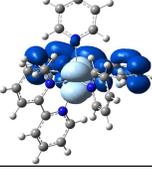
f = oscillator strength

Table A16. TDDFT triplet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MLCT geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
10	1.6656 (744.38)	0.0232	HOMO(A)→L+7(A) (18%) HOMO(A)→L+8(A) (17%) HOMO(A)→L+9(A) (23%)	IL (bpy→py)	
11	1.7282 (717.41)	0.0166	HOMO(A)→L+4(A) (11%) HOMO(A)→L+9(A) (56%)	LC/IL (bpy→py)	

f = oscillator strength

Table A17. TDDFT triplet-triplet transitions and corresponding electron difference density maps (EDDMs) calculated using the ³MC geometry of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/LanL2DZ/6-311G** level. In the EDDMs light blue indicates a decrease in electron density, while dark blue indicates an increase.

Tr.	E _{calc.} , eV (nm)	<i>f</i>	Composition	Character	EDDMs
3	1.9634 (631.47)	0.0060	HOMO(B)→L+3(B) (12%) HOMO(B)→L+6(B) (24%) HOMO(B)→L+9(B) (19%)	MC/MLCT (Ru→py/bpy)	
2	2.1356 (580.56)	0.0044	HOMO(A)→LUMO(A) (87%) HOMO(B)→L+1(B) (3%) HOMO(B)→L+6(B) (2%)	M(L)LCT (Ru(bpy/py)→bpy)	
5	2.7850 (445.17)	0.0290	H-1(B)→L+1(B) (19%) H-1(B)→L+3(B) (13%) H-1(B)→L+6(B) (22%) H-1(B)→L+9(B) (17%)	MLCT (Ru→bpy)	

f = oscillator strength

A4. Spin density surfaces

Table A18. Spin density surfaces and SOMO orbitals for the $^3\text{MLCT}$ geometry of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ calculated in water with the B3LYP and PBE0 functional.

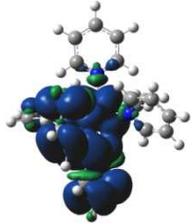
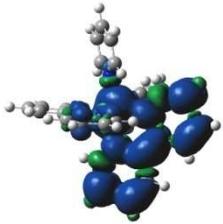
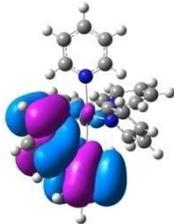
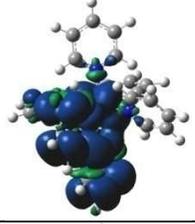
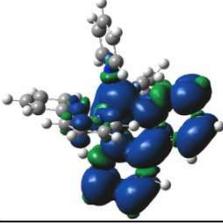
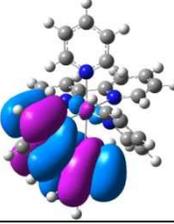
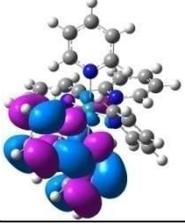
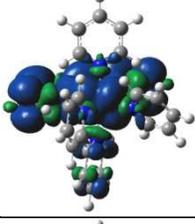
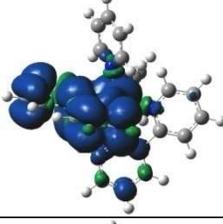
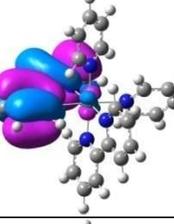
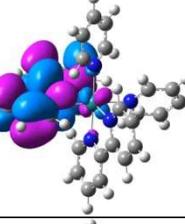
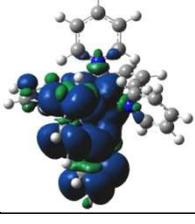
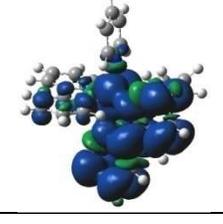
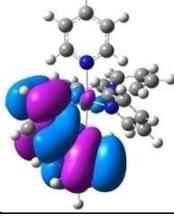
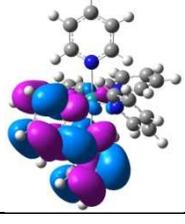
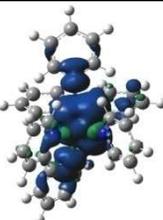
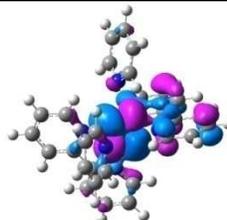
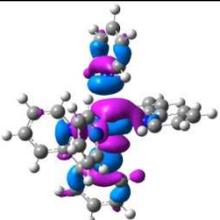
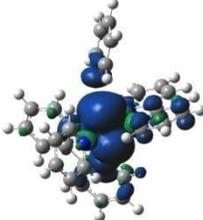
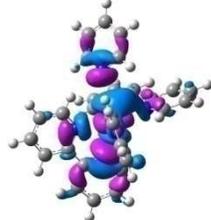
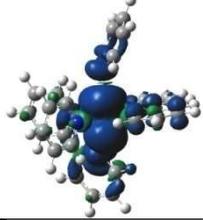
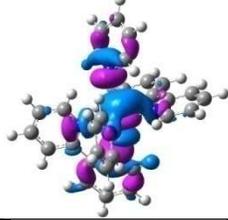
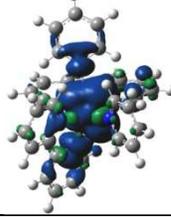
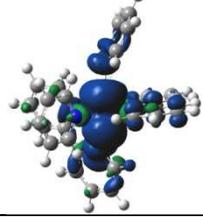
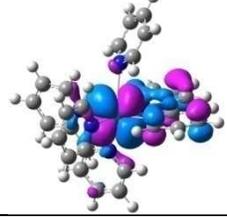
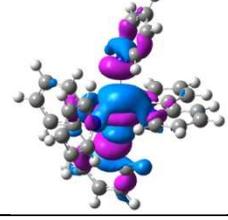
	Spin density		l-SOMO	h-SOMO
B3LYP LanL2DZ/6-31+G**				
B3LYP LanL2DZ/6-311G**				
PBE0 LanL2DZ/6-31+G**				
PBE0 LanL2DZ/6-311G**				

Table A19. Spin density surfaces and SOMO orbitals for the 3MC geometry of $cis-[Ru(bpy)_2(py)_2]^{2+}$ calculated in water with the B3LYP and PBE0 functional.

	Spin density		l-SOMO	h-SOMO
B3LYP LanL2DZ/6-31+G** <i>Gas phase</i>				
B3LYP LanL2DZ/6-311G**				
PBE0 LanL2DZ/6-31+G**				
PBE0 LanL2DZ/6-311G**				

A5. Triplet excited state energies

Table A20. Emission energy for the $^3\text{MLCT}$ state of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ calculated with the ΔSCF method in water.

	ΔSCF (eV)	ΔSCF (nm)
B3LYP		
LanL2DZ/6-31+G**	2.053	604
B3LYP		
LanL2DZ/6-311G**	1.997	621
PBE0		
LanL2DZ/6-31+G**	2.031	610
PBE0		
LanL2DZ/6-311G**	1.980	626

Table A21. Energy difference for the $^3\text{MLCT}$ and ^3MC states of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ in water.

	ΔE ($^3\text{MLCT}-^3\text{MC}$) (eV)
B3LYP	n.d.
LanL2DZ/6-31+G**	
B3LYP	0.458
LanL2DZ/6-311G**	
PBE0	0.309
LanL2DZ/6-31+G**	
PBE0	0.278
LanL2DZ/6-311G**	
TPSSH	0.144
LanL2DZ/6-311G**	
M06	0.624
LanL2DZ/6-311G**	
mPW1PBE	0.294
LanL2DZ/6-311G**	
mPW1LYP	0.540
LanL2DZ/6-311G**	
m062X	0.919
LanL2DZ/6-311G**	
HSEh1PBE	0.281
LanL2DZ/6-311G**	
Average	0.427
Standard Deviation	0.237

n.d.= not determined. All our attempts to optimize the ^3MC geometry at the B3LYP/6-31+G** with the CPCM solvent model were not successful.

Table A22. Energy difference for the $^3\text{MLCT}$ and ^3MC states of *cis*-[Ru(bpy)₂(py)₂]²⁺ in dichloromethane.

	$\Delta E (^3\text{MLCT}-^3\text{MC})$ (eV)
PBE0	0.294
LanL2DZ/6-311G**	
TPSSh	0.156
LanL2DZ/6-311G**	
M06	0.638
LanL2DZ/6-311G**	
m062X	0.929
LanL2DZ/6-311G**	
Average	0.504
Standard Deviation	0.348

A6. ECP dependence

Table A23. Calculated bond lengths for the singlet ground state (GS) and triplet ³MLCT and ³MC states of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water at the PBE0/6-311G** level. Solvent effects were included using the CPCM method. The LanL2TZ, LanL08 and SDD ECP were employed for the Ru atom.

Bond lengths – GS						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
PBE0/ SDD/6-311G**	2.06507	2.08024	2.06507	2.08024	2.12268	2.12268
PBE0/ LANL2TZ/6-311G**	2.07792	2.09338	2.07792	2.09338	2.13546	2.13546
PBE0/ LANL08/6-311G**	2.07793	2.09339	2.07792	2.09339	2.13546	2.13546
Bond lengths – ³ MLCT						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
PBE0/ SDD/6-311G**	2.02431	2.05460	2.06123	2.10166	2.12835	2.15409
PBE0/ LANL2TZ/6-311G**	2.03277	2.06379	2.07188	2.11492	2.13970	2.16717
PBE0/ LANL08/6-311G**	2.03278	2.06379	2.07189	2.11492	2.13970	2.16717
Bond lengths – ³ MC						
	Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
PBE0/ SDD/6-311G**	2.34561	2.14324	2.08619	2.07933	2.12780	2.81406
PBE0/ LANL2TZ/6-311G**	2.36307	2.16182	2.09947	2.09402	2.14031	2.80064
PBE0/ LANL08/6-311G**	2.36311	2.16183	2.09950	2.09403	2.14029	2.80034

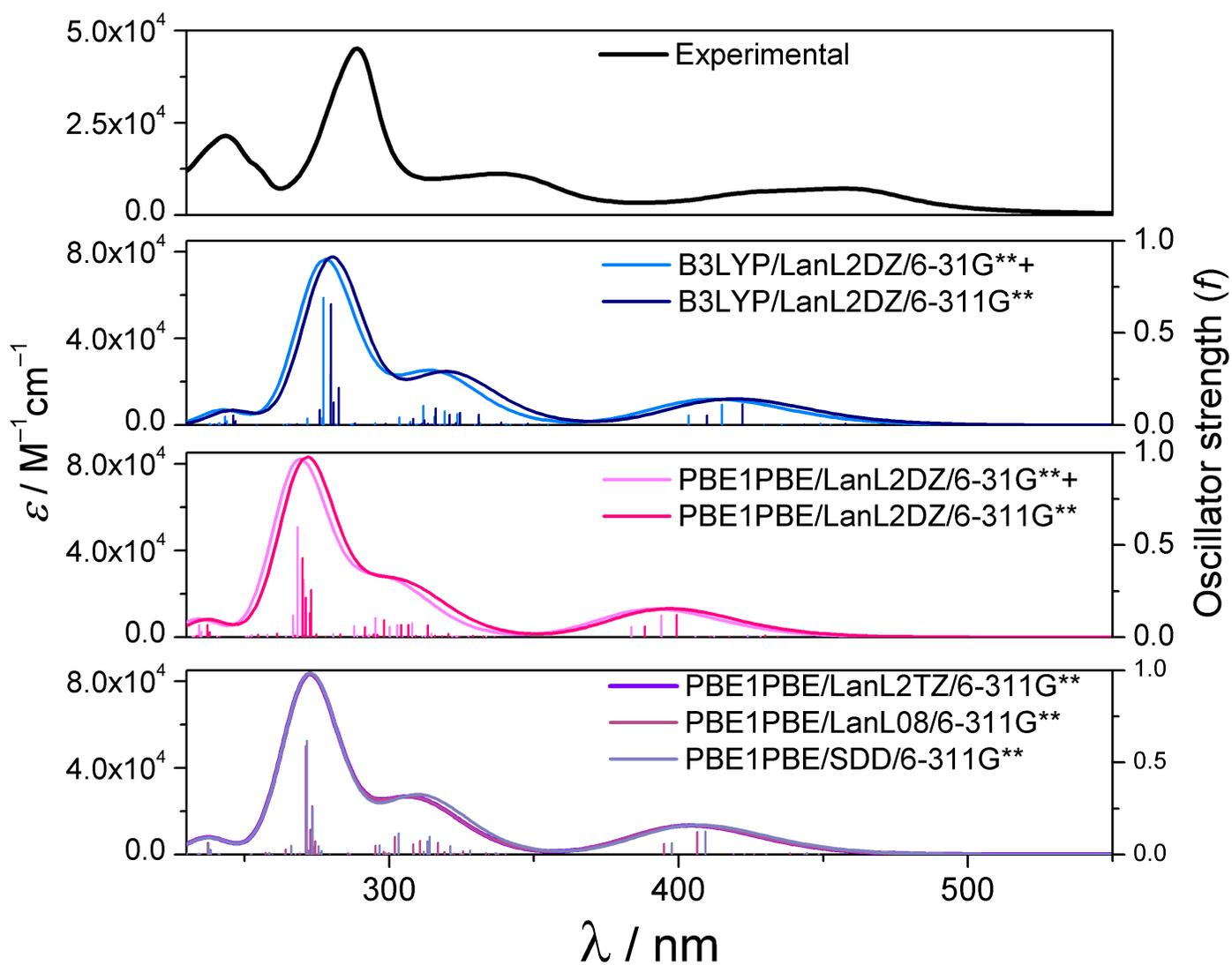


Figure A2. Experimental (black line) and calculated (colored lines) absorption spectra of *cis*-[Ru(bpy)₂(py)₂]²⁺ in water. The singlet excited transitions are shown as vertical bars with heights equal to the extinction coefficients. The theoretical curve was obtained using the program GAUSSSUM 1.05.

Table A24. Spin density surfaces and SOMO orbitals for the $^3\text{MLCT}$ geometry of $\text{cis}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ calculated in water at the PBE0/6-311G** level using the LanL2TZ, LanL08 and SDD ECP for the Ru atom.

	Spin density		l-SOMO	h-SOMO
PBE0/ SDD/6-311G**				
PBE0/ LANL2TZ/6-311G**				
PBE0/ LANL08/6-311G**				

Table A25. Spin density surfaces and SOMO orbitals for the ^3MC geometry of $\text{cis}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ calculated in water at the PBE0/6-311G** level using the LanL2TZ, LanL08 and SDD ECP for the Ru atom.

	Spin density		l-SOMO	h-SOMO
PBE0/ SDD/6-311G**				
PBE0/ LANL2TZ/6-311G**				
PBE0/ LANL08/6-311G**				

B – Optical Transient Absorption (OTA)

B1. Transient absorption results

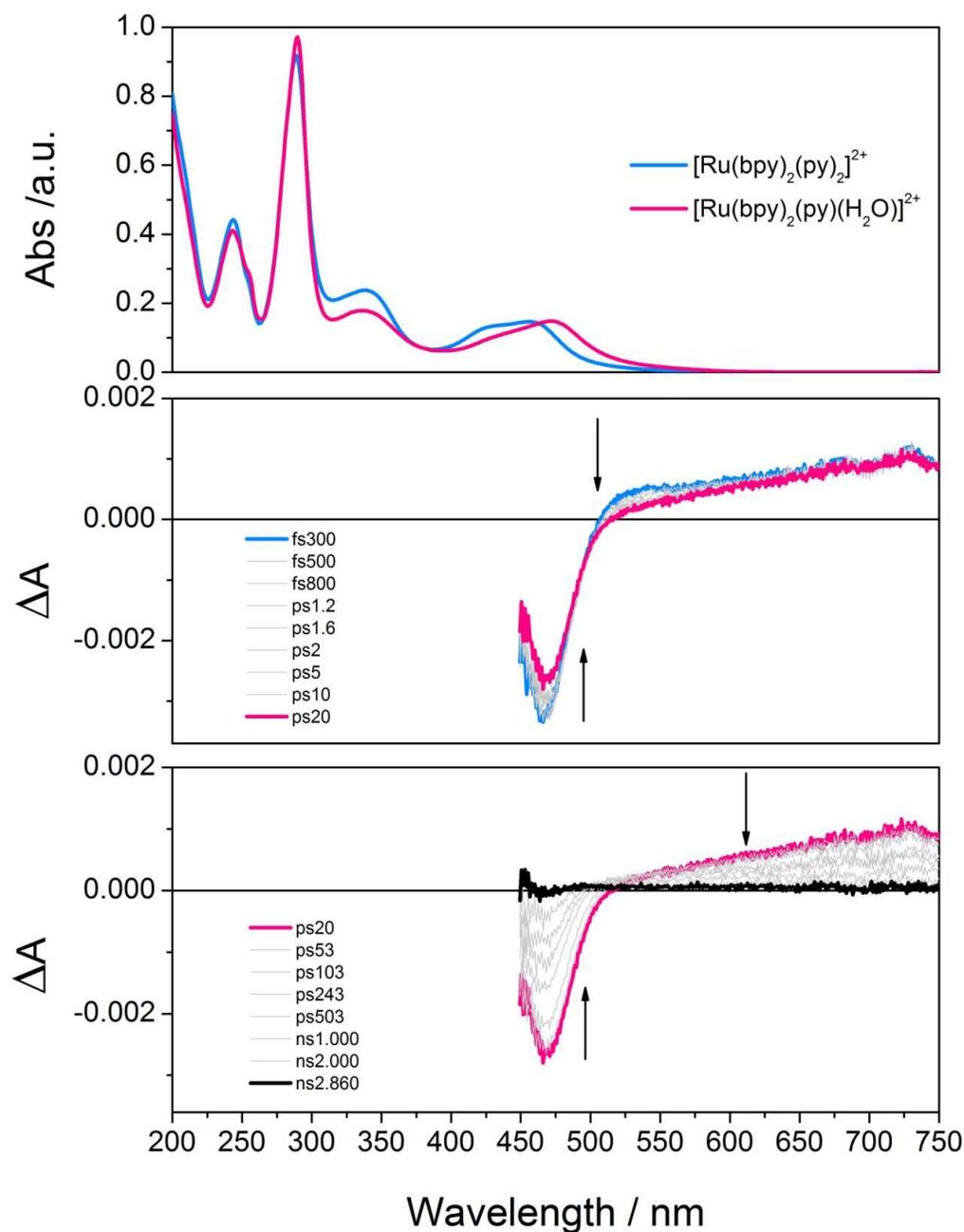


Figure B1. Top: UV-Vis absorption spectrum of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ (light blue) and $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})(\text{H}_2\text{O})]^{2+} + \text{py}$ (pink) in aqueous solution. The latter was obtained by photolysis of $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ with 420 nm light ($\lambda_{\text{exc}} = 420$ nm, 20 mW/cm^2 , 10 min). **Middle:** OTA spectra of aqueous $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ in the range 300 fs – 20 ps. **Bottom:** OTA spectra of aqueous $\text{cis-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ in the range 20 ps – 2.86 ns.

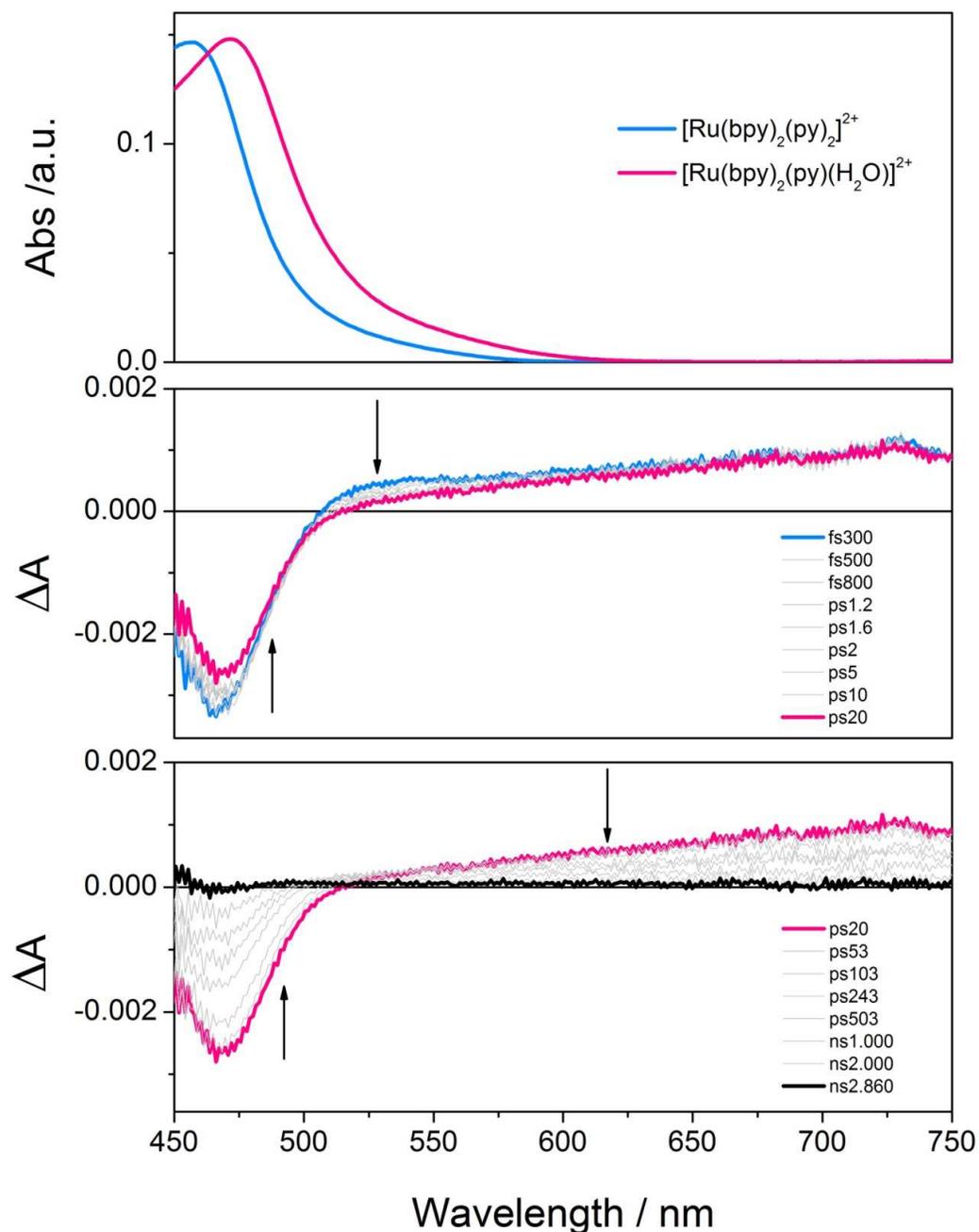


Figure B2. *Top:* Zoom in the UV-Vis absorption spectrum of $cis-[Ru(bpy)_2(py)_2]^{2+}$ (light blue) and $cis-[Ru(bpy)_2(py)(H_2O)]^{2+} + py$ (pink) in aqueous solution. The latter was obtained by photolysis of $cis-[Ru(bpy)_2(py)_2]^{2+}$ with 420 nm light ($\lambda_{exc} = 420$ nm, 20 mW/cm², 10 min). *Middle:* Zoom in the OTA spectra of aqueous $cis-[Ru(bpy)_2(py)_2]^{2+}$ in the range 300 fs – 20 ps. *Bottom:* Zoom in the OTA spectra of aqueous $cis-[Ru(bpy)_2(py)_2]^{2+}$ in the range 20 ps – 2.86 ns.

Table B1. Decay fitting parameters in the 467–723 nm range.

	467 nm	484 nm	651 nm	700 nm	723 nm
A1	-0.00137 ±0.00006	-0.00125 ±0.00004	0.00025 ±0.00003	0.00028 ±0.00003	0.0003 ±0.00003
τ₁(ps)	130±7	130±7	130±7	130±7	130±7
A2	-0.00187 ±0.00009	-0.00094 ±0.00006	0.00056 ±0.00005	0.00073 ±0.00006	0.00087 ±0.00006
τ₂(ps)	1700±200	1700±200	1700±200	1700±200	1700±200
A0	0.0002±0.0001	0.00037±0.00007	-0.00002±0.00005	-0.00005±0.00006	-0.00010±0.00007

Table B2. Decay fitting parameters in the 500–550 nm range.

	502 nm	517 nm	527 nm	540 nm
A3	0.00026 ±0.00001	0.00034 ±0.00001	0.00032 ±0.00001	0.00031 ±0.00001
τ₃(ps)	1.30±0.03	1.30±0.03	1.30±0.03	1.30±0.03
A0	-0.000360 ±5E-6	0.000060 ±8E-6	0.000170 ±5E-6	0.000220 ±5E-6

C – XTA

C1. XTA experimental setup

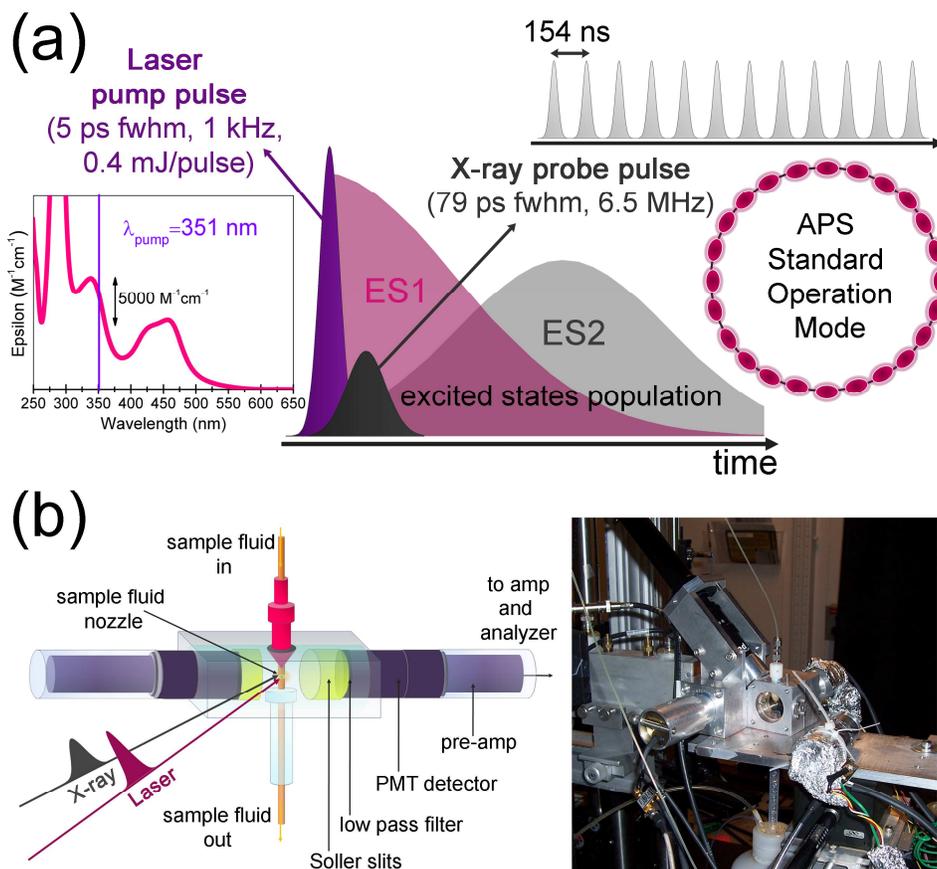


Figure C1. Experimental setup for XTA measurements at the APS 11ID-D beamline. (a) Pump/probe pulses features. (b) Detailed scheme (left panel) and photograph (right panel) of the sample cell, specifically designed for measurements on dilute solutions.

C2. XTA data acquisition and reduction strategy

For each selected time delay τ ($\tau = 150$ ps, 500 ps and 3000 ps) a series of 40 scans, each including (i) an ES spectrum from the fluoresce signals of the synchronized X-ray pulse at certain delay after the laser pump pulse excitation; (ii) a GS spectrum from fluorescence signals of the same X-ray pulse averaged over its 50 round trips in the storage ring prior to the laser pulse and (iii) a reference ruthenium metal foil spectrum for energy alignment, was collected. The solution (500 mL 1 mM) was replaced after ca. 3 h of laser irradiation, to avoid undesired photoproduct accumulation in the probed volume. Pre-edge region and XANES part of the spectra were acquired with a constant energy step of 5, 2 and 1 eV in the regions $E_{\text{edge}} - 150 \text{ eV} < E < E_{\text{edge}} - 30 \text{ eV}$, $E_{\text{edge}} - 30 \text{ eV} < E < E_{\text{edge}} - 15 \text{ eV}$, and $E_{\text{edge}} - 15 \text{ eV} < E < E_{\text{edge}} + 20 \text{ eV}$, respectively. The EXAFS part (from $k = 2 \text{ \AA}^{-1}$ up to 12 \AA^{-1}) was collected using a constant $\Delta k = 0.05 \text{ \AA}^{-1}$, resulting in a variable sampling step in energy. The integration time per point was of 4 s for the pre-edge and XANES regions and linearly variable from 5 to 30 s in the EXAFS part of the spectrum. The extraction of the $\chi(k)$ functions was

performed using the Athena programs.²⁰ After extraction, ES and GS spectrum for each scan were aligned using the reference metal foil, obtaining an array of $[\chi_i^{\text{GS}}(k), \chi_i^{\text{ES}}(k, \tau)]$ curves, for $1 < i < 40$ (number of scan). The difference spectra $\Delta\chi_i(k, \tau) = \chi_i^{\text{ES}}(k, \tau) - \chi_i^{\text{GS}}(k)$ were then computed for each scan, and then averaged on the 40 scans of a series, in k-space. The $\chi_i^{\text{GS}}(k)$ spectra acquired for all the scans and for each time delay were globally averaged to obtain an high-statistics GS spectrum, namely $\chi^{\text{GS}}(k)$, to be used as starting point for the differential analysis procedure (see Section C4).

The average $\Delta\chi(k, \tau)$ transient spectra are reported in Figure C2 for $\tau = 150, 500$ and 3000 ps (green, blue and pink circles, respectively). It is evident that, also if averaged on a number of acquisitions noticeably higher than that routinely used in EXAFS static experiments, the curves are characterized by a quite low signal-to-noise ratio. Notwithstanding the noisy appearance, the curves for the three selected delays differ significantly one from each other, especially in the intensity of the first differential oscillation and in the position of the minimum at ca. 2.7 \AA^{-1} . A Fourier filtering procedure was then applied to raw $\Delta\chi(k, \tau)$ curves: the EXAFS signal was first Fourier transformed from k- to R-space using the k range $2.5 \text{ \AA}^{-1} - 10.8 \text{ \AA}^{-1}$, and then was back-Fourier transformed into momentum space only in the R-range $1.0 \text{ \AA} - 5.0 \text{ \AA}$ (where the physical signal is expected). After the filtering operation, the momentum space will be named as q-space to be distinguished from the starting k-space. Filtered $\Delta\chi(q, \tau)$ and raw $\Delta\chi(k, \tau)$ differential spectra are separately compared for each time delay in Figure C2.

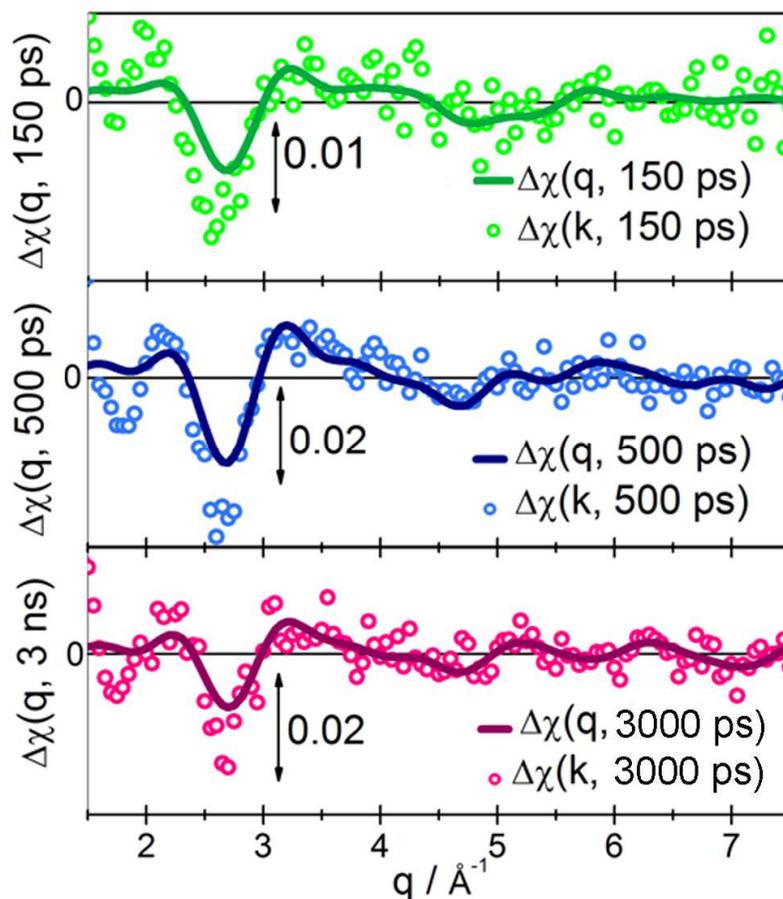


Figure C2. $\Delta\chi(k, \tau)$ transient spectra for $\tau = 150, 500$ and 3000 ps (green, blue and magenta circles, respectively) calculated as the average on all the scans of the differences $\Delta\chi_i(k, \tau) = \chi_i^{\text{ES}}(k, \tau) - \chi_i^{\text{GS}}(k, \tau)$ obtained for each scan, in k-

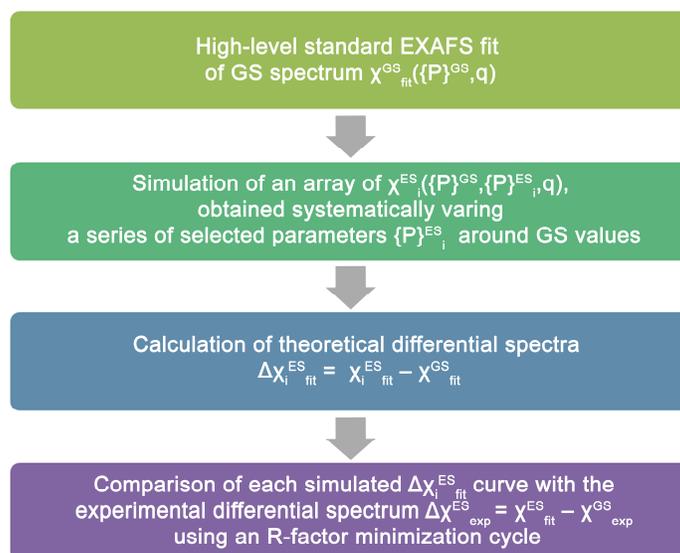
space. $\Delta\chi(k, \tau)$ differential spectra for each delay are compared with respective Fourier filtered $\Delta\chi(q, \tau)$ curves (k range 2.5 – 10.8 Å⁻¹ for the forward FT, R-range 1.0 – 5.0 Å for the backward FT), shown as dark green, dark blue and purple solid lines, respectively.

C3. Details on differential method for EXAFS structural refinement and its application to *cis*-[Ru(bpy)₂(py)₂]²⁺ photoreaction

It has recently been shown that the precision in determining structural parameters using XTA can be further enhanced by a quantitative structural analysis of the excited state.²¹ This approach is based on the fitting of the differential transient EXAFS spectrum directly in energy/momentum space by minimization of the square residual function between a large series of simulated differential EXAFS spectra and the experimental transient data. This method provides a superior accuracy for the derived structural parameters if compared to conventional EXAFS fitting methods, where structural modifications are extracted from the Fourier transform of the reconstructed excited-state EXAFS signal.²¹ EXAFS signals $\chi_i^{\text{ES}}(\{P\}_i, k)$ for a series of candidate excited state geometries, characterized by a set of parameters $\{P\}_i$ (bond lengths, Debye Waller parameters σ^2 , edge energy shift ΔE), are generated by using the FEFF6 code included in the IFEFFIT software package.²⁰ The simulated signals are converted into q-space, using the same k and R ranges adopted for the Fourier filtering of experimental data (see Section C2). Subsequently, the best fit curve $\chi_{\text{fit}}^{\text{GS}}(q)$ obtained from a standard EXAFS analysis of the GS EXAFS signal (see Section C4) is subtracted to each simulated $\chi_i^{\text{ES}}(\{P\}_i, q)$ spectrum. The resulting simulated differential spectra $\Delta\chi_i^{\text{ES}}(\{P\}_i, q)$ are compared with the experimental differential signal $\Delta\chi_{\text{exp}}^{\text{ES}}$ using the R-factor parameter defined by eq. (S1), where the index j runs from 1 to the total number of experimental points.

$$R_i = \sqrt{\frac{\sum_j (\Delta\chi_{\text{exp},j}^{\text{ES}} - \Delta\chi_{\text{fit},j}^{\text{ES}})^2}{\sum_j (\Delta\chi_{\text{exp},j}^{\text{ES}})^2}} \quad (\text{S1})$$

The procedure for EXAFS differential refinement is summarized in the following Scheme C1.



Scheme C1. Flow-chart for EXAFS data differential refinement.

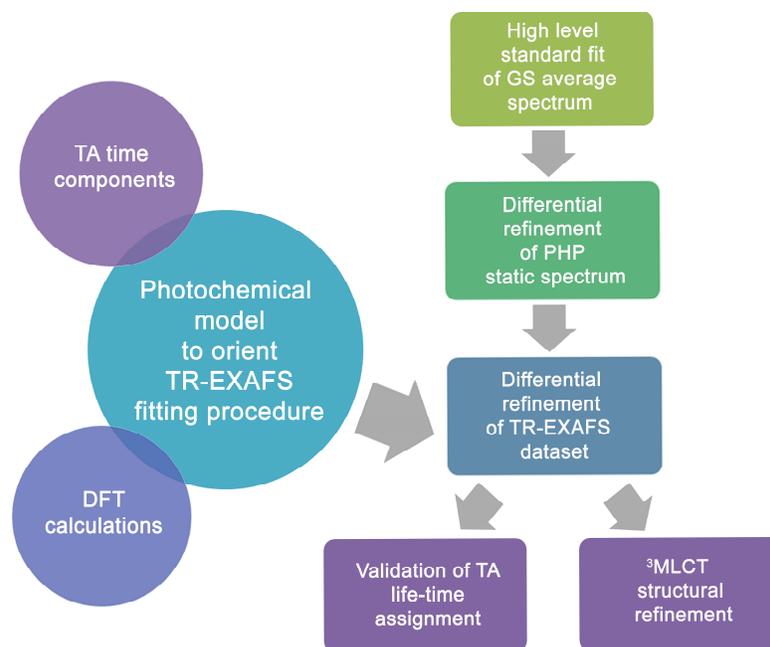
The photoreaction model proposed for $cis\text{-}[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ involves two excited states ($^3\text{MLCT}$ and ^3MC), each characterized by a specific set of structural distortions with respect to the GS geometry. In addition, a third set of independent parameters is required for the stable aquo photoproduct $cis\text{-}[\text{Ru}(\text{bpy})_2(\text{py})(\text{H}_2\text{O})]^{2+}$ (PHP). The structure of PHP is very similar to the GS one, at least from an EXAFS perspective. In fact, with the exception of some small distortion in the bond lengths, the first shell signal is expected to be only minimally perturbed after the substitution of the nitrogen of the dissociated py ring with the almost iso-electronic oxygen of the water molecule. The higher shells suffer of the signal loss due to lacking scattering paths related to a py ring, however the cumulative contribution of such paths can be estimated to be only 1/6 of the global signal (loss of 1 over 6 rings, 2 py rings and 4 rings associated in 2 bpy units).

A “one-shot” complete fitting model, simultaneously including all the possible intermediate structures, is not feasible (at least in the limit of available data quality) due to (i) the extremely high number of parameters needed, (ii) their not-negligible cross-correlations, (iii) the huge amount of machine and human time required to generate via FEFF all the $\chi^{\text{ES}}_j(\{\text{P}\}_j, q)$ spectra that such global model would require. The approach proposed here relies on a “step by step” strategy, based on the combination of optical (OTA) and structural X-ray based ultrafast techniques (XTA) with DFT calculations.

The main steps of data analysis are summarized in Scheme C2. First of all, an extremely accurate fit of the GS spectrum, namely $\chi^{\text{GS}}_{\text{fit}}(q)$ is obtained (more details in Section C4). The $\chi^{\text{GS}}_{\text{fit}}(q)$ spectrum is used in the calculation of the $\Delta\chi^{\text{ES}}_{\text{fit}}(\{\text{P}\}_i, q) = \chi^{\text{ES}}_{\text{fit}}(\{\text{P}\}_i, q) - \chi^{\text{GS}}_{\text{fit}}(q)$ simulated differences. Moreover, the parameters values obtained from the standard EXAFS fitting procedure provide the central nodes of the variation grid along each dimension in the N -dimensional space corresponding to N simultaneously varied parameters. The following step consists in the analysis of the static EXAFS spectrum of the PHP (see Section C5), using the differential method described above. This preliminary analysis is fundamental to obtain structural parameters for the PHP that can be employed in the analysis of the XTA data. Briefly, the two main reasons for adopting a differential approach are:

- (i) it is very difficult to discriminate two very similar structures as GS and PHP using an EXAFS standard approach. On the contrary, the use of a differential approach can provide an experimentally optimized structure for PHP, suitable for the subsequent interpretation of transient data;
- (ii) The application of the differential method to a static problem can be regarded as a feasibility test on a set of data characterized by a good signal-to-noise ratio, before starting the same kind of refinement on the more complex time-resolved dataset.

OTA measurements highlight the presence of two time components ($\tau_{\text{long}} = 1700$ ps and $\tau_{\text{short}} = 130$ ps). The longer component can be safely assigned to the $^3\text{MLCT}$ ES lifetime. Conversely, the interpretation of the shorter contribution is more controversial, however it can be tentatively related to the ^3MC /photochemistry pathway. Although OTA data alone are not informative on the photoinduced structural distortions of the complex, the synergic combination of OTA results and DFT calculation is useful to orient the fitting procedure of XTA data (see section C6). Moreover, XTA analysis provides in turn a feedback control on the longer OTA time-component assignment and elucidates the structural distortions in the $^3\text{MLCT}$ state.



Scheme C2. Schematic representation of the main steps of data analysis, based on the combination of OTA results with DFT calculations to orient the fitting procedure of XTA dataset.

C4. Details on GS spectrum EXAFS fit and comparison between static spectra of GS and aquo-photoproduct

An high-statistic GS spectrum $\chi_{\text{exp}}^{\text{GS}}(k)$ was obtained averaging the $\chi_i^{\text{GS}}(k)$ spectra acquired for all scans and all time delays. This average GS spectrum was FT filtered choosing for the backward and forward FT the same k and R ranges used to smooth the transient data ($2.5 - 10.8 \text{ \AA}^{-1}$; $1.0 - 5.0 \text{ \AA}$). Several trials were performed, systematically selecting the fitting space among k -, q - and R -space, and tuning the starting parameter values to get the best configuration in terms of fit goodness in q -space (where the XTA dataset has been analyzed) and physical meaningfulness of the parameters. The best results were obtained fitting in R -space, in the range $\Delta R = 1.0 - 5.0 \text{ \AA}$ ($2\Delta k\Delta R/\pi \sim 21$), the k -weighted FT function, in the $2.5 - 10.8 \text{ \AA}^{-1}$ k -range. The k -weighted FT functions for the experimental (black circles) and best fit spectra (gray solid lines) are reported in Figure C3a, for both the imaginary part (top panel) and the modulus (bottom panel). Phase and amplitude functions of each path were calculated by the FEFF code²⁰ using the DFT optimized GS structure (PBE0/LanL2DZ/6-311G**) as input. All the EXAFS paths up to $R = 5.0 \text{ \AA}$ have been included in the fitting model. To limit the number of optimized variables, all paths were optimized with the same amplitude factor (S_0^2) and with the same energy shift (ΔE) parameter. Moreover, both the pairs of py and bpy ligands were considered as rigid objects, whose only degree of freedom was the radial translation along the corresponding Ru–N axis. Consequently, the only two structural parameters optimized in the fit were the distances $R_{\text{Ru-N(py)}}$ and $R_{\text{Ru-N(bpy)}}$; the lengths of all the other paths were calculated starting from these two values, according to geometrical constraints imposed by the rigidity of the py and bpy rings. Concerning the Debye-Waller (DW) factors, only two parameters were optimized: $\sigma_{\text{N(py)}}^2$ and $\sigma_{\text{N(bpy)}}^2$, associated to Ru–N bonds for py or bpy ligands, respectively. For single scattering (SS) and multiple scattering (MS) paths

involving n atoms of the same ligand, we imposed the corresponding DW factor to be $\sigma^2 = n\sigma_{N(L)}^2$ ($L = \text{py}$ or bpy). Several almost co-linear MS paths involve two N atoms of two opposite L and L' ligands. In these cases DW factors were calculated as $\sigma_{\text{MS}}^2 = \sigma_{N(L)}^2 + \sigma_{N(L')}^2$. In summary, the fit runs over 6 independent parameters.

To demonstrate how the use of a differential approach is advantageous already in the static case analysis, we compared in Figure C3 the EXAFS spectra of the GS complex and of its aquo-photoproduct (PHP). The striking similarity between the two spectra can be noticed in the figure, where the normalized $\mu\chi(E)$ spectra for the GS (obtained as the average of all the laser-off acquisitions within the XTA dataset) and for the PHP (collected on the EXAFS beamline BM26 at the ESRF) are reported.²² The two experimental spectra plotted in q -space are compared in Figure C3c; spectrum $\chi_{\text{exp}}^{\text{GS}}(q)$ for the GS and spectrum $\chi_{\text{exp}}^{\text{PHP}}(q)$ for the PHP.

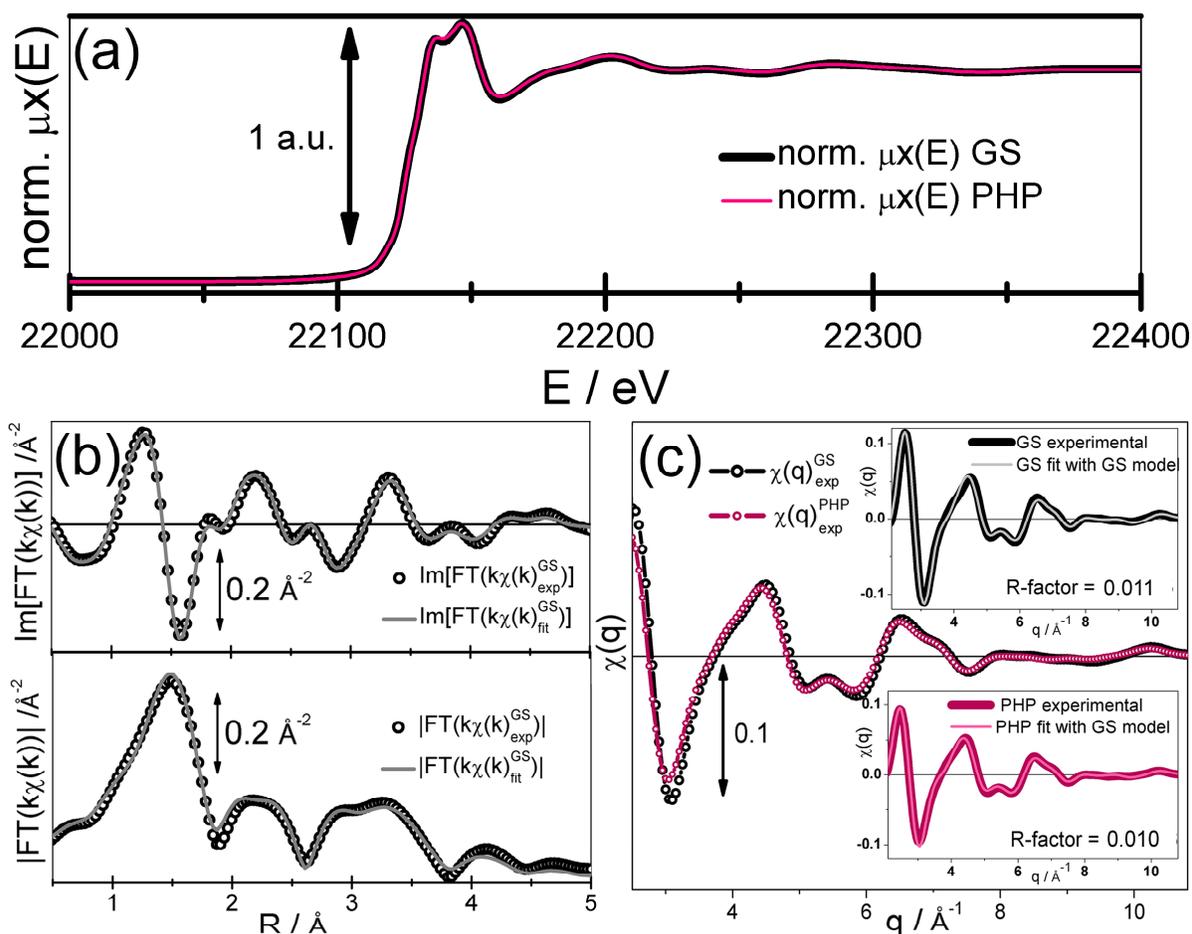


Figure C3. (a) Normalized $\mu\chi(E)$ spectra for GS (black solid line), obtained as the average of all the laser-off acquisitions within the XTA dataset, and for PHP (magenta solid line), collected on the EXAFS beamline BM26 at the ESRF. (b) Fitting of GS spectrum $\chi_{\text{exp}}^{\text{GS}}(q)$: k -weighted FT functions for the experimental (black circles) and best fit curves (gray solid lines) are reported both for the imaginary part (top panel) and the modulus (bottom panel). (c) Comparison between $\chi_{\text{exp}}^{\text{GS}}(q)$ for GS and $\chi_{\text{exp}}^{\text{PHP}}(q)$ for PHP. In the upper inset: best fit $\chi_{\text{exp}}^{\text{GS}}(q)$ (gray thin line) compared with $\chi_{\text{exp}}^{\text{GS}}(q)$ experimental spectrum (black thick line); in the bottom inset: test fit on the $\chi_{\text{exp}}^{\text{PHP}}(q)$ spectrum, using exactly the same conditions adopted in the case of the $\chi_{\text{exp}}^{\text{GS}}(q)$ spectrum fit, in terms of selected fitting-space, number and features of included paths and parameters starting values.

To confirm the inadequacy of a standard EXAFS fitting procedure in discriminating among the GS and PHP structures, a test fit was performed on the $\chi^{\text{PHP}}_{\text{exp}}(q)$ spectrum, using exactly the same conditions adopted for the $\chi^{\text{GS}}_{\text{exp}}(q)$ spectrum fitting, in terms of selected fitting-space, number and parametrization of included paths and starting values (see Insets of Figure C3c). In this case the coordination number for the N(py) atoms imposed in the fit ($N_{\text{py}}^{\text{fit}}$) is thus equal to two, and differs from the effective coordination number $N_{\text{py}}^{\text{eff}} = 1$, being one py unit substituted by the H₂O molecule. This fit is characterized by an R-factor value of $\sim 1\%$, as in the case of the $\chi^{\text{GS}}_{\text{exp}}(q)$ best fit, and by refined parameters values perfectly comparable with the ones found for the $\chi^{\text{GS}}_{\text{exp}}(q)$ curve, within their experimental error. The effective missing of a py unit in the PHP structure is well compensated by a slight increase of the associated DW factor σ^2_{py} , from $(0.0032 \pm 0.0008) \text{ \AA}^2$ to $(0.0041 \pm 0.0009) \text{ \AA}^2$. The results are reported in Table C1, and are fully compatible with what obtained from previous EXAFS static studies on the same and on very similar complexes.²³⁻²⁵

Table C1. Results from EXAFS analysis of GS and PHP spectra $\chi^{\text{GS}}_{\text{exp}}(k)$ and $\chi^{\text{PHP}}_{\text{exp}}(k)$. The fits were performed in R-space in the $\Delta R = 1.00 - 5.00 \text{ \AA}$ range, over k-weighted FT of the $\chi(k)$ functions in the $2.5 - 10.8 \text{ \AA}^{-1}$ range. A single ΔE_0 and a single S_0^2 have been optimized for all SS and MS paths. Coordination numbers for N(L) atoms, where L = py or bpy, are reported, distinguishing between values imposed in the fit (N_L^{fit}) and effective values (N_L^{eff}). The same structural model of the GS complex was employed in the photoproduct test fit, thus in this case $N_{\text{py}}^{\text{fit}} = 2 \neq N_{\text{py}}^{\text{eff}} = 1$. Both fits are characterized by a very good R-factor value, $\sim 1\%$, and give parameters values almost identical in the limit of their errors. $R_{\text{N(L)}}$ bond distances in the GS DFT-PBE0 optimized structure are reported for comparison, separately averaged for each type of ligand L.

Results of GS EXAFS fit and test fit on PHP using GS model			
Parameters	GS DFT average bond lengths	GS EXAFS fit	PHP tentative EXAFS fit
Independent points		21	21
Number of variables		6	6
R-factor		0.011	0.010
S_0^2		0.95 ± 0.06	0.94 ± 0.06
ΔE (eV)		0.8 ± 0.5	-0.4 ± 0.6
$R_{\text{N(py)}} (\text{\AA})$	2.14	2.09 ± 0.03	2.12 ± 0.03
$\sigma^2_{\text{N(py)}} (\text{\AA}^2)$		0.0032 ± 0.0008	0.0041 ± 0.0009
$N_{\text{py}}^{\text{fit}} (N_{\text{py}}^{\text{eff}})$		2 (2)	2 (1)
$R_{\text{N(bpy)}} (\text{\AA})$	2.08	2.05 ± 0.02	2.04 ± 0.01
$\sigma^2_{\text{N(bpy)}} (\text{\AA}^2)$		0.0026 ± 0.0008	0.0023 ± 0.0008
$N_{\text{bpy}}^{\text{fit}} (N_{\text{bpy}}^{\text{eff}})$		4 (4)	4 (4)

C5. Details on PHP differential EXAFS analysis

The PHP structure has been primarily modeled simply removing from the set of SS and MS paths generated for the GS structure all the paths related to one of the two py rings, except for that involving the first shell N atom, maintained to simulate the almost isoelectronic O atom of the water molecule coordinated to the metal centre. The fitting model is identical to that described in Section C4 for the GS spectrum, apart from the use of two additional parameters to account for the newly coordinated solvent molecule, i.e. the bond distance $R_{\text{Ru-O(H}_2\text{O)}}$ and the oxygen DW σ^2_{O} .

Fixing the amplitude S_0^2 at the GS value, the array of parameters P is then composed in the following way: $P = \{\Delta E, \Delta R_{\text{bpy}}, \Delta R_{\text{py}}, \Delta R_{\text{O}}, \sigma^2_{\text{bpy}}, \sigma^2_{\text{py}}, \sigma^2_{\text{O}}\}$, where the parameters ΔR_L indicates the bond length variations from the DFT-optimized structure for ligands L = bpy, py and H₂O respectively. Our application of the differential method is based on the computation of a series of variational grids for a sub-set of parameters P',

with the remaining parameters fixed to the GS best fit values: $P_{GS} = \{\Delta E = 0.8 \text{ eV}, \Delta R_{bpy} = -0.03 \text{ \AA}, \Delta R_{py} = -0.05 \text{ \AA}, \Delta R_O = \Delta R_{py} = 0.05 \text{ \AA}, \sigma_{bpy}^2 = 0.0026 \text{ \AA}^2, \sigma_{py}^2 = 0.0032 \text{ \AA}^2, \sigma_O^2 = \sigma_{py}^2\}$. Operationally, we selected a subspace P' of dimension N' , planning a series of reasonable values for the variation of each parameter (centered on the GS value for that parameter). Hence, we computed a N' -dimensional grid where the i^{th} node is a simulated $\chi_i^{\text{PHP}}(q)$ curve, characterized by the parameters $P_i = \{P'; P_{GS}\}$ and obtained by summing the scattering paths for the PHP structure calculated via the FEFF code, setting the parameters to selected values. The minimization of the R-factor between the experimental differential curve $\Delta\chi_{\text{exp}}^{\text{PHP}}(q) = \chi_{\text{exp}}^{\text{PHP}}(q) - \chi_{\text{exp}}^{\text{GS}}(q)$ and each of the simulated differential spectra $\Delta\chi_i^{\text{PHP}}(q) = \chi_i^{\text{PHP}}(q) - \chi_{\text{fit}}^{\text{GS}}(q)$ is performed using a dedicated script. The minimization results can be represented in terms of R-factor(p_1, \dots, p_N) surfaces, where N is the number of parameters effectively varied.

The simultaneous exploration of the whole 7-dimensional parameter space with reasonable ranges for the variation of the parameters is not feasible, due to the extremely high human and machine time demand that such operation would require. However, supported by DFT calculations and general considerations about the “natural” correlations expected among the parameters, it is possible to properly select an informative sequence of subspaces P' to be scanned. We explored a consecutive series of four 2D or 3D sub-spaces, with (a) $P' = \{P_{GS}; \Delta E; \Delta R_{bpy}\}$; (b) $P' = \{P_{GS}; \Delta R_O, \sigma_O^2\}$; (c) $P' = \{P_{GS}; \sigma_O^2 = 0.0055 \text{ \AA}^2, \Delta E, \Delta R_{bpy}, \Delta R_O\}$; (d) $P' = \{P_{GS}; \Delta R_{py}, \Delta R_O\}$, trying to approach the global minimum in the whole 7D space.

After the partial minimization cycles (a) – (d), an extended exploration of the 4D space including the energy shift and the three distortions along the bonds Ru–N(bpy), Ru–N(py) and Ru–O(H₂O), i.e. $P' = \{P_{GS}; \sigma_O^2 = 0.0055 \text{ \AA}^2, \Delta E, \Delta R_{bpy}, \Delta R_{py}, \Delta R_O\}$, was performed. DW values were fixed to GS values for bpy and py units, while the DW accounting for vibrations along the Ru–O(H₂O) bond was set to the value $\sigma_O^2 = 0.0055 \text{ \AA}^2$, obtained from the minimization cycle (b). Among the 258 $\Delta\chi_i^{\text{PHP}}(q)$ simulated and tested curves, the lower R-factor value of 0.147 is obtained in correspondence of the array $\{P_{GS}; \sigma_O^2 = 0.0055 \text{ \AA}^2, \Delta E = -1.0 \text{ eV}, \Delta R_{bpy} = -0.03 \text{ \AA}, \Delta R_{py} = -0.07 \text{ \AA}, \Delta R_O = -0.02 \text{ \AA}\}$. The $\Delta\chi_i^{\text{PHP}}(q)$ calculated in correspondence of these values is then selected as best differential fit for the experimental $\Delta\chi_{\text{exp}}^{\text{PHP}}(q)$ and will be hereinafter mentioned as $\Delta\chi_{\text{fit}}^{\text{PHP}}(q)$.

Table C2 compares (i) $R_{\text{Ru-N(L)}}$ bond distances (where L = bpy, py or H₂O) from DFT geometry optimization of GS and PHP, separately averaged for each type of ligand, see also Section A; (ii) GS standard EXAFS fitting results; (iii) parameters' values obtained using the differential method for the PHP structural refinement.

Table C2. Results from standard EXAFS analysis of GS and from differential analysis of PHP spectrum (parameters P' selected for variation are highlighted in red). DFT-PBE0 first shell $R_{\text{Ru-N(L)}}$ bond distances (where L= bpy, py, H₂O) for GS and PHP, separately averaged for each type of ligand L, are reported for comparison. The error on PHP refined parameters corresponds to the step separating two contiguous nodes on the minimization grid employed.

Optimized Parameters for GS and PHP				
Parameters	DFT optimization		EXAFS fit	
	GS average bond lengths	PHP average bond lengths	GS (Standard analysis)	PHP (Differential analysis)
Independent points			21	-
Number of variables			6	5 refined variables
R-factor			0.011	0.147*
S_0^2			0.95 ± 0.06	0.95 ± 0.06
ΔE (eV)			0.8 ± 0.5	-1.0 ± 0.5
R_{bpy} (R_{bpy}) (Å)	2.08	2.07	2.05 ± 0.02	2.05 ± 0.01
σ_{bpy}^2 (Å ²)			0.0026 ± 0.0008	0.0023 ± 0.0008
R_{py} (R_{py}) (Å)	2.14	2.13	2.09 ± 0.03	2.07 ± 0.01
σ_{py}^2 (Å ²)			0.0032 ± 0.0008	0.0041 ± 0.0009
R_{O} (R_{O}) (Å)	-	2.21	-	2.12 ± 0.01
σ_{O}^2 (Å ²)			-	0.005 ± 0.001

*R-factor defined according to eq. (S1), not directly comparable with the fit goodness figure reported for GS standard EXAFS fit.

Differential refinement indicates an almost unvaried bond length for the bpy rings with respect to the GS value, while the bond length for the remaining py ring appears to be contracted from 2.09 Å to 2.07 Å. For the newly coordinated water molecule, a noticeable increase on Ru–O(H₂O) bond length of 0.03 Å with respect to the average Ru–N(py) GS bond distance is obtained. Such feature is associated with an increase of the corresponding DW, from $\sigma_{\text{py}}^2 = (0.0032 \pm 0.0008) \text{ \AA}^2$ to $\sigma_{\text{O}}^2 = (0.005 \pm 0.001) \text{ \AA}^2$, in good agreement with the substitution of a py ring with a smaller and more vibrationally-active water ligand.

DFT-optimized geometries are key starting points for the analysis, especially when working close to the state-of-art sensitivity limit of the XAS technique and when the complexity of the case of study unavoidably requires some approximations (e.g. choosing a meaningful variation range for a structural parameter, or defining a priority scale for testing different kinds of distortions). Moreover, the theoretical results can also be used as a final test for the reliability of the experimental data interpretation, in a synergic cross-comparison useful to make us aware of specific limits and advantages for each approach.

In the studied case, a systematic slight underestimation of the EXAFS-refined bond lengths is found respect to the values from DFT geometry optimization, as already obtained for this complex and other analogues.^{25, 26}

Hence, a more meaningful comparison can be done focusing on relative variations moving from GS to PHP structure, rather than on the absolute values. The more striking result is the good DFT/ EXAFS agreement in pointing out the elongation of the PHP Ru–O(H₂O) bond respect to previous GS py. Regarding the bond distortions of the py and bpy ligands, DFT average values indicates a slight contraction for both ligand types, while, as mentioned before, the differential EXAFS refinement points out an almost unvaried bond length for the bpy rings with respect to the GS value, and a more evident -0.02 \AA contraction along the Ru–N(py) bond. Checking the DFT Ru bond lengths separately for each first-shell neighbor (see Table A2), it is possible to realize how the bond distances for all the rings belonging to the two bpy units are almost unchanged, except the one of the ring in *trans* position to the water-substituted py (containing the N atom labeled as N1, see Scheme A1). Imaging to separate a bpy unit in two independent py rings, the major

changes foreseen by DFT can be summarized in an elongation of the Ru–O(H₂O) bond and in a contraction of the Ru–N1 bond involving the ligand in *trans* position.

However, the model adopted for EXAFS data interpretation optimizes the distortions for the two N(bpy) atoms with a single ΔR_{bpy} parameter, and does not account for independent distortions along each of the Ru–N(bpy) bond axis. A major limit of this approach, adopted to limit the number of parameters, relies in the difficulty in discriminating between single py rings and pairs of rings grouped in bpy units “artificially” tied in an identical motion. Therefore, the pronounced contraction ΔR_{py} is likely to be associated to the bond contraction for the single ring in *trans* to O (H₂O) of a bpy unit, and it has not been correctly assigned due to the vinculum on ΔR_{bpy} . This hypothesis is also supported by the strong anti-correlation found between ΔR_{py} and ΔR_{O} .

Finally, in Figure C4a are reported the six possible 2D cuts of the 4D R-factor surface as a function of the parameter array (ΔE , ΔR_{bpy} , ΔR_{py} , ΔR_{O}), obtained by fixing to the values found in correspondence of the minimum a couple of parameters each time. The high quality of the fit can be appreciated in Figure C4b, where the experimental differential spectrum $\Delta\chi_{\text{exp}}^{\text{PHP}}(q)$ (black circles) is compared with the $\Delta\chi_{\text{fit}}^{\text{PHP}}(q)$ best fit curve (magenta solid line). Finally, in Figure C4c, a comparison between the not-differential GS and PHP experimental spectra with their respective best fit curves $\chi_{\text{fit}}^{\text{GS}}(q)$ and $\chi_{\text{fit}}^{\text{PHP}}(q)$ is reported.

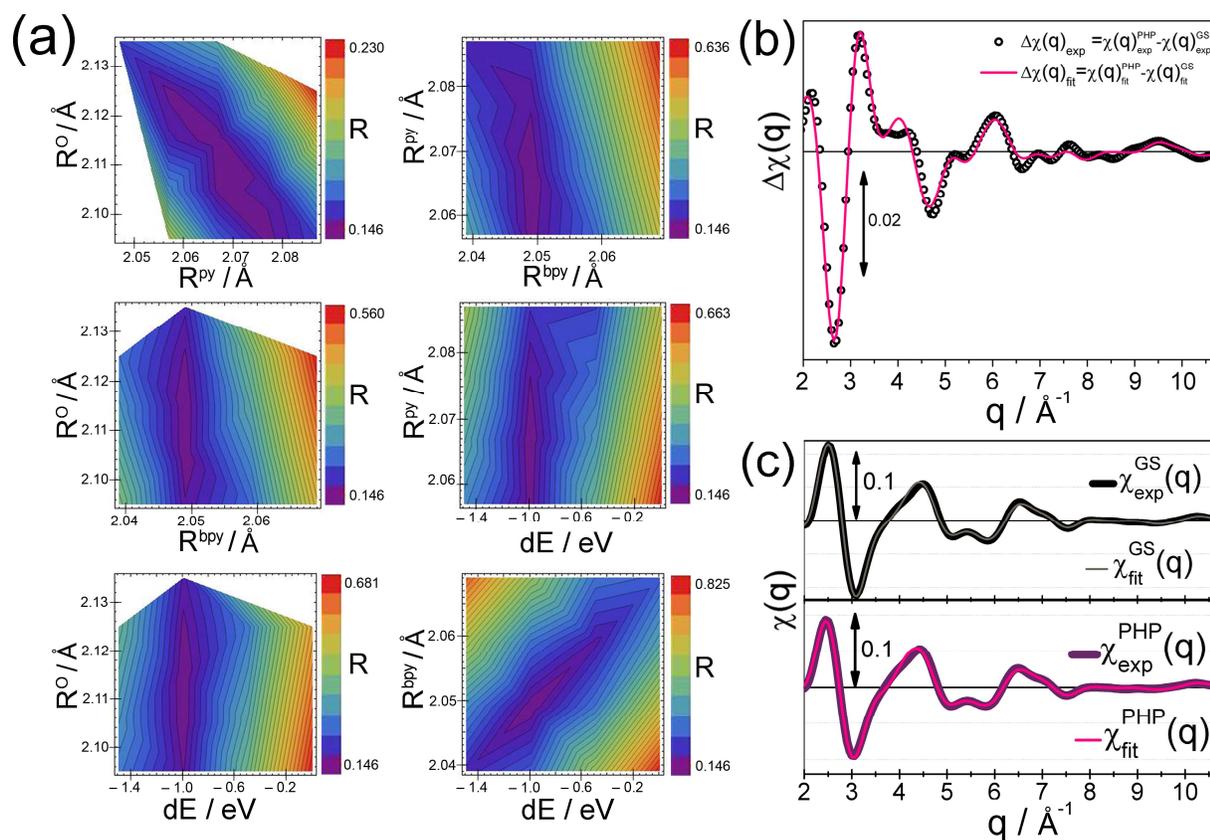


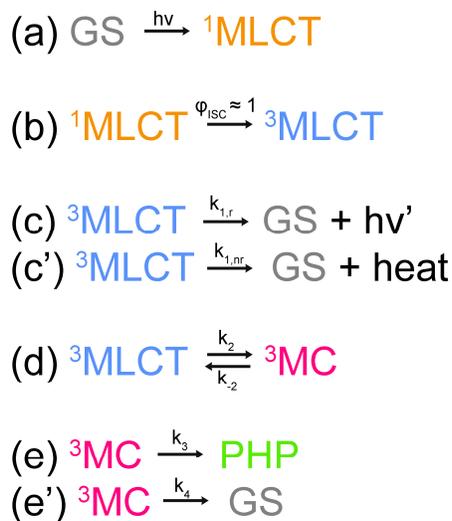
Figure C4. Results from the final minimization procedure of the PHP differential EXAFS analysis, in the 4D space $P' = \{P_{\text{GS}}; \sigma_{\text{O}}^2 = 0.0055 \text{ \AA}^2, \Delta E, \Delta R_{\text{bpy}}, \Delta R_{\text{py}}, \Delta R_{\text{O}}\}$. (a) 2D cuts of the 4D R-factor (ΔE , ΔR_{bpy} , ΔR_{py} , ΔR_{O}) surface, obtained by fixing couples of parameters each time to the values found in correspondence of the minimum. (b) Comparison between experimental differential spectrum $\Delta\chi_{\text{exp}}^{\text{PHP}}(q)$ (black circles) and $\Delta\chi_{\text{fit}}^{\text{PHP}}(q)$ best-fit curve (pink solid line). (c) Comparison between the not-differential GS (upper part) and photoproduct (bottom part) experimental

spectra with correspondent best fit curves $\chi_{\text{fit}}^{\text{GS}}(q)$ and $\chi_{\text{fit}}^{\text{GS}}(q)$, obtained from standard EXAFS fit and differential EXAFS refinement respectively.

C6. Details on XTA fitting procedure

C6.1. Excited state dynamics

A widely accepted general scheme for the excited-state dynamics of ruthenium polypyridyl complexes is the following:



Scheme C3

In the specific case of aqueous *cis*-[Ru(bpy)₂(py)₂]Cl₂, $k_{1,r}$ and $k_{1,nr}$ (eq. c and c' in Scheme C3) can be considered as negligible. Moreover $k_{-2} \ll k_2$, resulting in irreversible population of the ³MC state from the ³MLCT.²⁷⁻³⁰ According to such a scenario and considering the OTA time components together with a 20% photochemical yield ϕ , the populations of the ³MLCT ES and PHP species, that mainly contribute to XTA signal at the investigated time-points, can be calculated using the set of equations (S2) and represented as in Figure C5:

$$\begin{aligned} N_{3MLCT} &= \exp\left(-\frac{t}{\tau_{long}}\right) \\ N_{PHP} &= \phi[1 - N_{3MLCT} - \Delta(\tau_{short})] \end{aligned} \quad \text{(S2)}$$

The $\Delta(\tau_{short})$ parameter is related to the shorter OTA time component, and is given by eq. (S3):

$$\Delta(\tau_{short}) = \exp\left(-\frac{t}{\tau_{short}}\right)(1 - N_{3MLCT}) \quad \text{(S3)}$$

$\Delta(\tau_{\text{short}})$ is a minor correction, that slightly delays the PHP formation along the relaxation cascade from $^3\text{MLCT}$ ES. Its effect can be appreciated only at the earlier time-delay investigated (150 ps) and it is negligible for the following delays $\tau = 500$ ps and 3000 ps, that actually provide the more reliable structural information. Such effect can be tentatively related to the ^3MC /photochemistry pathway, and eventually to complex solvent-mediated interactions. However, further investigation is needed to confirm this assignment.

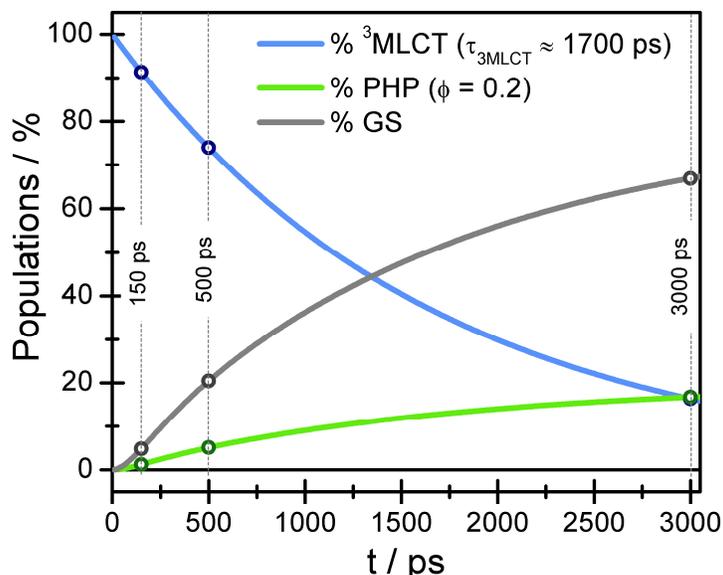


Figure C5. Time evolution of $^3\text{MLCT}$ population (blue solid line) and PHP percentage (green solid line) calculated according to Scheme C3 and eqs (S2). Circles and vertical dashed lines are placed in correspondence of the XTA experimental time delays.

Such information was employed to orientate the XTA differential fitting procedure. Briefly, the optimized amplitudes f^{PHP} and f^{MLCT} relative to the PHP and $^3\text{MLCT}$ components of the XTA signal were searched within an interval defined by the estimated populations. In particular, the ratio $f^{\text{PHP}}/f^{\text{MLCT}}$ was constrained to vary around the population ratio $R^{\text{MLCT/PHP}}$ calculated using eqs. (S2) and assuming a tolerance of $\pm 0.2 R^{\text{MLCT/PHP}}$ with respect to the center of the range (vide infra, in particular Section C6.5). In this way a considerable stabilization in the fit outcomes was achieved.

The population of $^3\text{MLCT}$ and the PHP percentage estimated for the three time-delays investigate by XTA (150 ps, 500 ps and 3000 ps), according to eqs (2), are reported in Table C3.

Table C3. Population of $^3\text{MLCT}$ and PHP percentage for $\tau = 150$ ps, 500 ps and 3000 ps, estimated using eqs. (S2), according to the assignment $\tau_{\text{MLCT}} = \tau_{\text{long}} = 1700$ ps for the longer OTA component. The ratio $R = \% \text{ES}(\tau_{\text{long}}) / \% \text{PHP}$ is used to orient the XTA fitting procedure (see also Section C6.5).

Time-delay (ps)	% $^3\text{MLCT}$ (τ_{long})	% PHP	$R^{\text{ES/PHP}} = \% \text{ES}(\tau_{\text{long}}) / \% \text{PHP}$ $[(R^{\text{ES/PHP}} - 0.2 R^{\text{ES/PHP}}) : (R^{\text{ES/PHP}} + 0.2 R^{\text{ES/PHP}})]$
150	91.3	1.2	76 [61:91]
500	73.9	5.1	15 [13:18]
3000	16.3	16.7	1.0 [0.8:1.2]

C6.2. Detailed description of XTA fitting results

As mentioned before, we developed a fitting strategy based on the combination of the two dominant structural components, i.e. the PHP and the long-lived ³MLCT ES. The possibility of a slightly different energy shift due to the use of different beamlines to acquire the static PHP spectrum and the XTA dataset was considered by repeating the fit in correspondence of different ΔE values for the PHP simulated $\chi_{\text{fit}}^{\text{PHP}}(q)$ curve.

The fitting procedure, implemented using a dedicated script, can be summarized in the steps listed below. For a selected time delay τ and a selected value of PHP energy shift ΔE_i^{PHP} :

- (i) The experimental $\Delta\chi(q, \tau)$ curve, as well as the simulated $\chi_{\text{fit}}^{\text{PHP}}(\Delta E_i^{\text{PHP}}, q)$ and $\chi_{\text{fit}}^{\text{GS}}(q)$ curves are imported, and the theoretical PHP component $\Delta\chi^{\text{PHP}}(\Delta E_i^{\text{PHP}}, q) = \chi_{\text{fit}}^{\text{PHP}}(\Delta E_i^{\text{PHP}}, q) - \chi_{\text{fit}}^{\text{GS}}(q)$ is calculated.
- (ii) An array of $\chi_{\text{ES}}^{\text{ES}}(\text{P}_{\text{GS}}; \text{P}', q)$ simulated curves (ES = ³MLCT), obtained from systematic distortions of the GS structure the in the parameter subspace P' is imported.
- (iii) the experimental $\Delta\chi(q, \tau)$ curve is fitted with a linear combination of PHP and long-lived ES contributions for each $\chi_{\text{ES}}^{\text{ES}}(\text{P}_{\text{GS}}; \text{P}', q)$ curve, i.e. $\Delta\chi(q, \tau) = f_i^{\text{PHP}}\Delta\chi^{\text{PHP}}(\Delta E_i^{\text{PHP}}, q) + f_i^{\text{ES}}\Delta\chi_{\text{ES}}^{\text{ES}}(\text{P}_{\text{GS}}; \text{P}', q)$, where $\Delta\chi_{\text{ES}}^{\text{ES}}(\text{P}_{\text{GS}}; \text{P}', q) = \chi_{\text{ES}}^{\text{ES}}(\text{P}_{\text{GS}}; \text{P}', q) - \chi_{\text{fit}}^{\text{GS}}(q)$ and the amplitudes f_i^{PHP} and f_i^{ES} are the optimized variables; a R_i R-factor is calculated for each simulated ES structure.

The minimum R_i value is used to select the best fit for the experimental $\Delta\chi(q, \tau)$ curve and to determine the optimized values of P' parameters and amplitudes f^{PHP} and f^{ES} . A complete overview on the fitting results is reported in Table C4.

Table C4. Detailed report on results from the 30-fits differential refinement procedure of XTA data. For all investigated time delays, the optimized values obtained for bond lengths $R_{\text{Ru-N1}}$, $R_{\text{Ru-N53}}$, for PHP and ES energy shifts (ΔE^{PHP} and ΔE^{ES} , respectively) and for amplitudes f^{PHP} and f^{ES} related to PHP and ES component (as well as the value of the ratio $R^{\text{ES/PHP}}$) are listed.

Optimized parameters values from differential fitting procedure of XTA data						
$\tau_{3\text{MLCT}} = \tau_{\text{long}}$						
τ (ps)	$R_{\text{Ru-N1}}$ (Å)	$R_{\text{Ru-N53}}$ (Å)	ΔE^{PHP} ΔE^{ES} (eV)	f^{PHP} f^{ES} ($R^{\text{ES/PHP}}$)	R-factor	
150	2.07	2.06	-1.99 -1.49	0.002 0.134 (67.0)	0.284	
500	2.03	2.20	0.49 -0.99	0.020 0.271 (13.5)	0.180	
3000	2.03	2.16	-0.99 -0.99	0.084 0.100 (1.2)	0.378	

C6.3. Repetition of the fitting-procedure assuming $\tau_{\text{long}} = \tau_{3\text{MC}}$

As a final test, we explored the effect of a reversal assignment of OTA time-component, i.e. $\tau_{3\text{MC}} = \tau_{\text{long}} = 1700$ ps, on the XTA fitting results. For the sake of clarity, hereinafter we will indicate as model (1) the previously

discussed assignment, $\tau_{3\text{MLCT}} = \tau_{\text{long}} = 1700$ ps, and as model (2) the one corresponding to the reversal assignment $\tau_{3\text{MC}} = \tau_{\text{long}} = 1700$ ps.

A comparison between the fitting results obtained using model (1) or (2) is depicted in Figure C5. Here, the R-factor values found for corresponding fits are plotted as a function of the only parameter associated to the PHP component i.e. its energy shift ΔE_i^{PHP} . Every point in the plots is thus associated with a minimum in the sub-space $P' = \{P_{\text{GS}}; \Delta E^{\text{ES}}, R_{\text{Ru-N1}}, R_{\text{Ru-N53}}\}$, separately explored for $^3\text{MLCT}$ (model (1), blue points in Figure C5) and ^3MC (model (2), purple points in Figure C5) geometries. For more details on the selection of the structural parameters to refine and their variation grids, see the following Section C6.4.

Maintaining the ΔE_i^{PHP} value inside a reasonable range for variation, the two series of fits are very well-separated for all the three time delays analyzed, and the fit goodness is systematically higher (lower R-factor values) in the case of model (1). This evidence allows to definitely assign the longer OTA time component $\tau_{\text{long}} = 1700$ ps to the $^3\text{MLCT}$ ES.

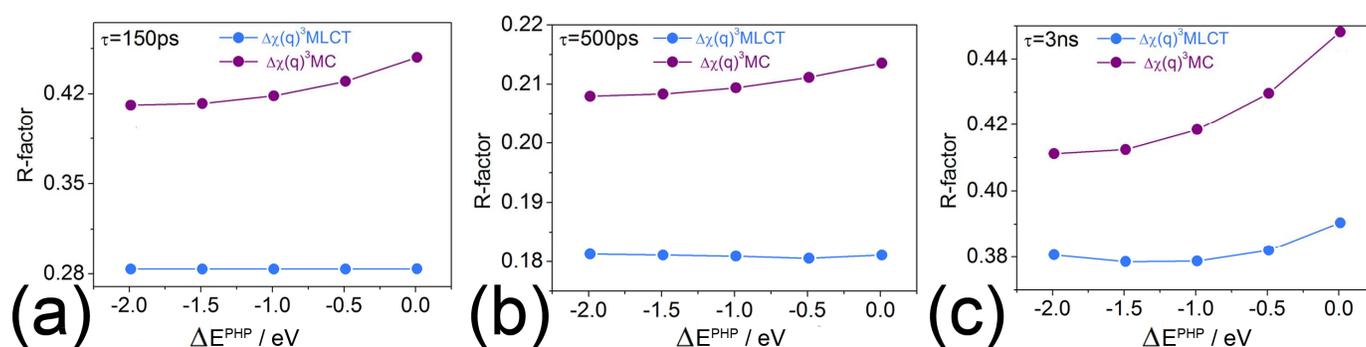


Figure C5. Results from the complete XTA fitting procedure, separately reported for each time delay (150, 500 and 3000 ps in part (a), (b) and (c), respectively). The R-factor value for each fit is plotted as a function of the only parameter associated to the PHP component, i.e. its energy shift ΔE_i^{PHP} .

C6.4. Minimization grids selected to model and optimize $^3\text{MLCT}$ and ^3MC structures

The approach adopted for differential refinement of the time-resolved dataset was that already discussed in details for PHP differential analysis (see Section C5). In the case of XTA analysis, the DFT role in directing the selection of what bond lengths preferentially modify is fundamental. However, the differential approach guarantees an independent experimental validation for the theoretical geometries. In Table C5 Ru first-shell bond distances from DFT geometry optimization of $^3\text{MLCT}$ and ^3MC ES structures are summarized (see also Section A). Analyzing the values reported in Table C5, it can be noticed that the main variations occur in correspondence of Ru–N1(bpy) and Ru–N53(py) bonds, for both the considered ES structures. Also the Ru–N2 bond is perturbed but, to limit the number of parameters, the selection of bonds to be systematically modified was restricted to Ru–N1(bpy) and Ru–N53(py) only. Starting from the EXAFS paths generated for the GS structure, we isolated the SS and MS paths involving the 6+6 atoms of the two rings selected, carefully adjusting the paths degeneracy, and varied independently the two bond distances $R_{\text{Ru-N1}}$ and $R_{\text{Ru-N53}}$.

Table C5. Ru first-shell bond distances from DFT geometry optimization of $^3\text{MLCT}$ and ^3MC structures, distinguishing all the 6 bonds in which the Ru-center is involved. Bonds distances selected for variational minimization are highlighted in red.

$^3\text{MLCT}$ structural parameters from DFT geometry optimization					
Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
2.03	2.06	2.07	2.11	2.14	2.17
^3MC structural parameters from DFT geometry optimization					
Ru–N1(bpy)	Ru–N2(bpy)	Ru–N13(bpy)	Ru–N14(bpy)	Ru–N42(py)	Ru–N53(py)
2.37	2.16	2.10	2.09	2.14	2.80

The explored sub-space P' is constituted for both the possible ESs by $P' = \{P_{\text{GS}}; \Delta E^{\text{ES}}, R_{\text{Ru-N1}}, R_{\text{Ru-N53}}\}$; the $\{R_{\text{Ru-N1}}, R_{\text{Ru-N53}}\}$ variation grids for the $^3\text{MLCT}$ and ^3MC ESs are composed in the following way: (i) $^3\text{MLCT}$ variation grid (employed for the principal model (1)) comprises $R_{\text{Ru-N1}}$ values from 2.00 Å to 2.22 Å in steps of 0.02 and $R_{\text{Ru-N53}}$ values from 1.96 Å to 2.24 Å in steps of 0.02; (ii) ^3MC variation grid (employed for the final check using model (2)) includes $R_{\text{Ru-N1}}$ values from 2.15 Å to 2.45 Å in steps of 0.05 Å and $R_{\text{Ru-N53}}$ values from 2.55 Å to 3.15 Å in steps of 0.1 Å. The bond length distortions subspace is complemented with a wide-range ΔE^{ES} scan, from – 2.0 eV to 2.0 eV, meshed in 0.5 eV steps. The fitting procedure was repeated for each time delay, using a set of 5 values for ΔE_i^{PHP} , comprised in the – 2.0 – 0.0 eV and regularly spaced of 0.5 eV.

C6.5. Constrains for the optimization of f^{PHP} and f^{ES} amplitudes

An important point to be discussed involves the definition of some constrains for the optimization of f^{PHP} and f^{ES} amplitudes, to stabilize the fitting procedure and to orient the results towards chemically meaningful values, according to estimated populations. Indeed, the main features of simulated $\Delta\chi^{\text{ES}}$ curves (maxima and minima positions and overall curve shape) are quite similar for all the states/species here considered, i.e. ES = $^3\text{MLCT}$ in the principal model (1), ^3MC in the control model (2), and PHP (at least considering the portions of the variation grids near to DFT theoretical values). The striking difference relies in the amplitude of the $\Delta\chi^{\text{ES}}$ curves, especially comparing the simulated spectra $\Delta\chi^{\text{MLCT}}$ and $\Delta\chi^{\text{PHP}}$ with $\Delta\chi^{\text{MC}}$, where the highly pronounced structural distortions cause a huge increase in the differential amplitude. This can explain why a completely not-constrained two components fits for the amplitude optimization was found to be very unstable, due to the high correlation between f^{PHP} and f^{ES} amplitudes guessed in the fit. We decided to employ the percentages calculated using eqs (2) to orient the fit procedure. The ratio $R^{\text{ES/PHP}} = \% \text{ES} (\tau_{\text{long}}) / \% \text{PHP}$ accounted for the relative amplitude expected between the two components included in the fit, and was used to define the fit constrains, overcoming the problem on the unknown excitation yield (acting as a global scale factor for the experimental $\Delta\chi(q, \tau)$ curve). The amplitudes f^{PHP} and f^{ES} were constrained to vary around the calculated value of $R^{\text{ES/PHP}}$, assuming a tolerance of $\pm 0.2 R^{\text{ES/PHP}}$ with respect to the centre of the range. We obtained in this way a considerable stabilization in the fit outcomes.

C6.4. Graphical representation of XTA fit results for $\tau = 150$ ps

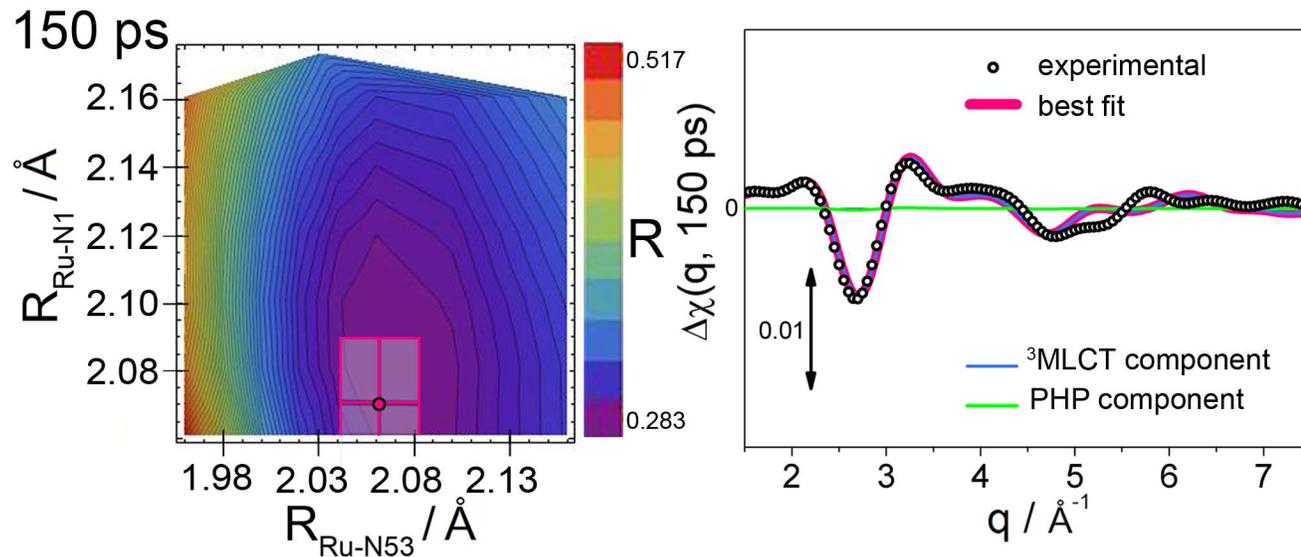


Figure C6. Surface contour plots of the fit R-factor as a function of $R_{\text{Ru-N1}}$ and $R_{\text{Ru-N53}}$ and best fit $\Delta\chi_{\text{fit}}(q, \tau)$ curves corresponding to the R-factor surface global minimum (magenta solid lines), superimposed to experimental XTA data (black circles) for $\tau = 150$ ps. The magenta box identifies the experimental error interval (± 0.02 \AA on both $R_{\text{Ru-N1}}$ and $R_{\text{Ru-N53}}$ axis) around the minimum localized at the lines' crossing point. The fit components relative to the $^3\text{MLCT}$ and PHP contributions to the overall XTA signal are indicated as blue and green solid lines respectively.

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