

SUPPORTING INFORMATION

for

A Photoinduced Mixed Valence Photoswitch

Agustina Cotic,^{a,b} Simon Cerfontaine,^c Leonardo Slep,^{a,b} Benjamin Elias,^c Ludovic Troian-Gautier,^c * and Alejandro Cadranel^{a,b,d,e} *

^a Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Inorgánica, Analítica y Química Física, Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

^b CONICET – Universidad de Buenos Aires, Instituto de Química-Física de Materiales, Medio Ambiente y Energía (INQUIMAE), Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

^c Université catholique de Louvain (UCLouvain), Institut de la Matière Condensée et des Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1, bte L4.01.02, 1348 Louvain-la-Neuve, Belgium

^d Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Physical Chemistry I, Egerlandstr. 3, 91058, Erlangen, Germany.

^e Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Interdisciplinary Center for Molecular Materials, Egerlandstr. 3, 91058, Erlangen, Germany.

*Correspondence to: Ludovic.Troian@uclouvain.be, acadranel@qi.fcen.uba.ar

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Experimental Details

Dp^{4+} was available from a previous study.¹ UV-visible-NIR spectra were recorded with an AvaSpec 2048 spectrometer. Spectroelectrochemical measurements were performed with an OTTLE cell. Ultrafast transient absorption experiments were conducted using an amplified Ti:sapphire fs laser system (Clark MXR CPA2101 and CPA2110, 1kHz, FWHM = 150 fs, $\lambda^{\text{exc}} = 460$ nm, 300-700 nJ per pulse) with TA pump / probe Helios (fsTAS) or EOS (nsTAS) detection system from Ultrafast Systems. In fsTAS experiments, white light was generated focusing a fraction of the fundamental 775 nm output onto a 2 mm sapphire disk (~430–760 nm) or a 1 cm sapphire disk (~800–1600 nm). In nsTAS experiments, white light (~370 to >1600 nm) was generated by a built-in photonic crystal fiber supercontinuum laser source with a fundamental of 1064 nm at 2 kHz output frequency and pulse width of approximately 1 ns. A magic angle configuration between the pump and the probe beams was employed to avoid rotational dynamics. Excitation pulses were generated by a NOPA. Bandpass filters with ± 5 or ± 10 nm were used to ensure low spectral width and to exclude 775 nm photons. Typical excitation spot areas are around 500 μm^2 and ensured to be larger than those of the probe beam. All measurements were conducted in a 2 mm quartz cuvette under argon atmosphere and continuous magnetic stirring, using solutions with absorbances of 0.5-0.7. To analyze transient absorption data, we used a suggested procedure.² We start with SVD and global analysis, using an all-sequential decay model that provides evolution associated spectra of potentially intervening species, to determine the number of decaying species that participate in the decay cascade. However, this doesn't necessary yield differential spectra with genuine physicochemical meaning. Afterwards, a target analysis is applied, using specific target models that result in species associated spectra with true physicochemical meaning. Obtained data were treated by SVD, global and target analyses using the R-package TIMP and GloTarAn.²⁻⁴

Density Functional Theory (DFT) was employed to fully optimize the species which are subject of their current report. The calculations were performed with *Gaussian 09*⁵ using Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang and Parr formalized as the B3LYP hybrid functional⁶⁻⁹ and the effective core potential basis set LanL2DZ implemented in G09,⁵ which describes first row elements using Dunning's D95V basis set and the Los Alamos ECP plus DZ basis for the heavier elements.¹⁰⁻¹³ Tight SCF convergence criteria were used along the geometry optimizations. No symmetry constraints were imposed. The Polarizable Continuum Model (PCM) approximation was used along the computations to account for solvation. The nature of the stationary points obtained in the optimization procedures was checked by means of vibrational analyses. Electronic spectra were computed by (TD)DFT, involving at least 130 excited states at the same level of theory.

In order to deconvolute the contribution of the two expected transitions in the NIR region of the excited triplet state of Dp^{4+} , we performed a least-squares fit of the spectral signal. A model involving 3 gaussian-shaped bands was employed, with the third one included to account for the spectral overlap with other transitions centered at higher energies. The fitting procedure was restricted to the range between 6150 to 13500 cm^{-1} , without imposing any constraints on the fitting parameters.

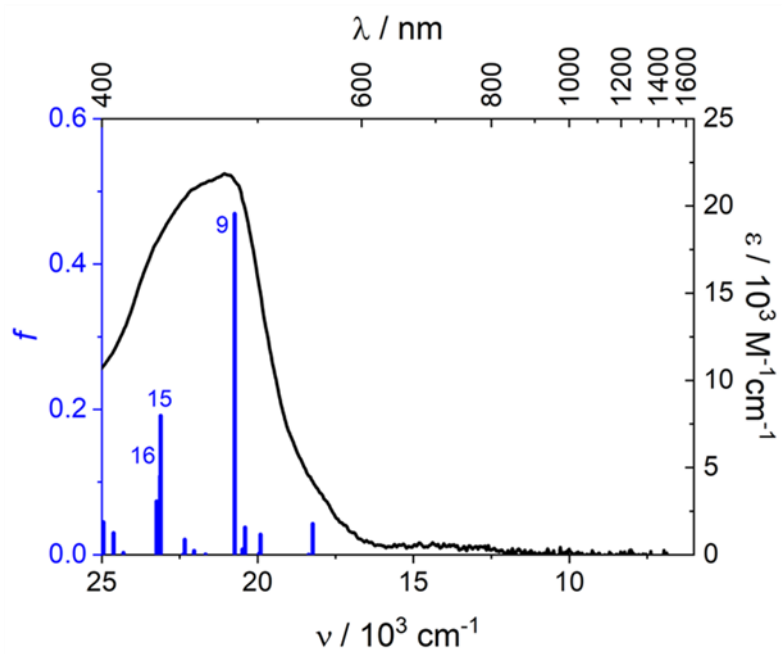


Figure S1. Calculated electronic transitions (blue bars) and experimental absorption spectrum (black curve) for Dp^{4+} .

Table S1. Selection ($f > 0.1$) of calculated electronic transitions for the optimized singlet state of Dp^{4+} .

No.	Energy / cm^{-1}	Osc. Strength	Major contribs	Assignment
9	20739	0.4692	H-4->LUMO (11%) H-2->LUMO (60%)	MLCT (Ru→Lp)
15	23113	0.1913	H-5->L+5 (11%) H-4->L+2 (24%) H-3->L+1 (15%) H-2->L+4 (17%)	MLCT (Ru→bpy)
16	23128	0.1085	H-5->L+4 (11%) H-4->L+1 (15%) H-3->L+2 (24%) H-2->L+5 (17%)	MLCT (Ru→bpy)

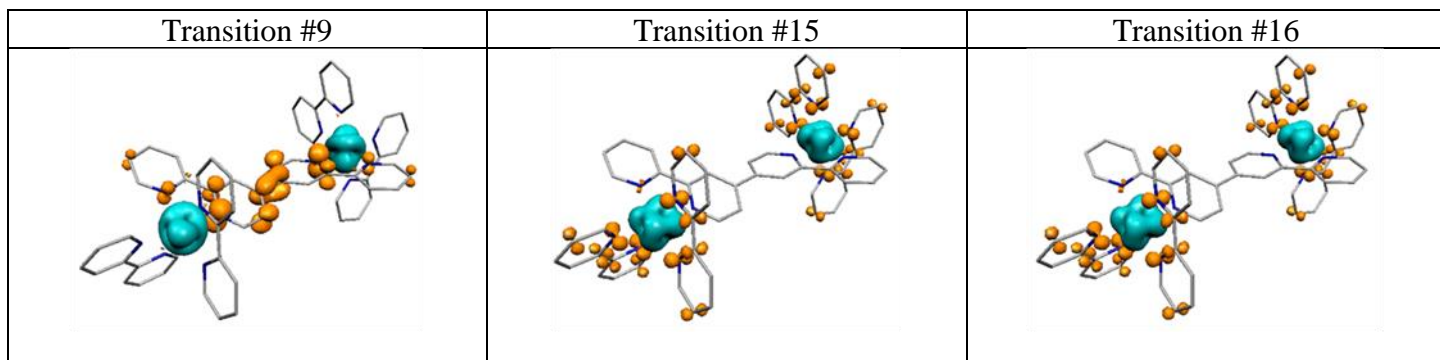


Figure S2. EDDMs (cutoff isovalue = 0.002) for transitions 9, 15 and 16 ($f > 0.1$) for the singlet ground state of Dp^{4+} . Cyan indicates loss and orange indicates gain of electron density for each transition.

Atom	X	Y	Z	Atom	X	Y	Z
Ru	-5.65650900	0.07386200	-0.00712700	C	0.74289200	0.00998500	-0.12734300
C	-2.86271900	-1.16424500	-0.42402200	C	1.46669600	1.18414500	-0.44024300
C	-8.55203600	0.19586900	1.06100400	C	1.48895200	-1.14522900	0.18545900
C	-5.24898300	-0.00581000	3.05164200	C	2.86272400	1.16412300	-0.42425500
C	-2.89214100	1.11214000	0.18223600	H	0.96568600	2.10493800	-0.71580500
C	-8.26095800	0.83648700	-1.19479500	C	2.89216200	-1.11214800	0.18243000
C	-5.73911000	-2.07808900	2.02605400	H	0.97932400	-2.06133300	0.45608900
C	-3.74238800	2.27679400	0.50168000	H	3.43137700	2.05115400	-0.66815000
C	-6.04225100	-2.76289900	0.75340700	N	3.57581100	0.04513100	-0.12087400
C	-7.28723800	1.03163900	-2.28733300	C	3.74242100	-2.27673600	0.50208500
C	-5.96148900	3.04238600	0.77232200	C	3.24520800	-3.55983000	0.79346400
C	-6.31043900	-2.50230100	-1.57990900	C	5.96152900	-3.04224800	0.77289800
C	-5.01554100	0.87597000	-2.91892900	C	4.13932900	-4.60217000	1.08277200
C	-1.46669000	-1.18428100	-0.44000900	H	2.17931400	-3.75170300	0.79329400
C	-9.93388200	0.41193300	0.98724900	C	5.52136800	-4.33762800	1.07326700
C	-5.15500200	-0.60597100	4.31370100	H	7.01585700	-2.79965100	0.75718100
C	-1.48893100	1.14521200	0.18525100	H	3.76619100	-5.59546600	1.30878500
C	-5.65410300	-2.73285200	3.26819800	H	6.24778400	-5.11248200	1.29064600
C	-9.64248000	1.06681200	-1.32594700	N	5.09769400	-2.02847900	0.49378600
C	-3.24516200	3.55993400	0.79283400	Ru	5.65652100	-0.07388100	-0.00711000
C	-7.63005900	1.49887000	-3.56932800	C	5.01558800	-0.87656200	-2.91876700
C	-6.31938800	-4.13824300	0.64975700	C	7.28728400	-1.03206800	-2.28712600
C	-5.52131400	4.33781600	1.07245600	C	5.30037600	-1.33639100	-4.21064200
C	-6.58928400	-3.86532900	-1.74150700	H	4.00594400	-0.61894000	-2.62709400
C	-5.30031500	1.33553900	-4.21090000	C	7.63011700	-1.49957000	-2.53902000
H	-5.10222000	1.05902200	2.92710600	C	6.63082000	-1.65431500	-4.54207000
H	-8.08771000	-0.14106500	1.97811200	H	4.49703000	-1.44069900	-4.93117900
H	-3.43138000	-2.05131700	-0.66775100	H	8.65808000	-1.74174300	-3.80967500
H	-6.29542900	-1.83062700	-2.42809400	H	6.88452500	-2.01399200	-5.53372500
H	-4.00590400	0.61838500	-2.62719800	C	6.04219100	2.76301700	0.75294200
H	-7.01582000	2.79980500	0.75662900	C	6.31037200	2.50203400	-1.58033200
H	-10.55060600	0.23522000	1.861122300	C	6.31927800	4.13835300	0.64905500
H	-4.92677900	0.00351400	5.18079900	C	6.58916700	3.86504400	-1.74216300
H	-0.96568800	-2.10512900	-0.71539700	H	6.29537300	1.83021700	-2.42840300
H	-6.79730500	-4.25553800	-2.73137700	C	6.59532900	4.69822800	-0.60786600
H	-4.49696300	1.43969000	-4.93145300	H	6.32370600	4.76608800	1.53157300
H	-6.24772200	5.11272100	1.28967600	H	6.79716800	4.25509300	-2.73210100
N	-3.57579800	-0.04519100	-0.12085200	H	6.81087800	5.75758900	-0.69904200
N	-5.53584600	-0.71888300	1.92833600	N	5.98203900	-0.72354300	-1.97291600
N	-7.72698500	0.40263600	-0.00149800	N	6.04040100	1.95587800	-0.36336300
N	-5.09766400	2.02855100	0.49341400	C	8.26099600	-0.83666200	-1.19462800
N	-5.98200000	0.72316000	-1.97305300	C	9.64253200	-1.06693200	-1.32574100
N	-6.04044000	-1.95594900	-0.36303400	C	10.48986200	-0.85396500	-0.22753900
C	-6.63075400	1.65340500	-4.54240400	H	10.05605100	-1.40598700	-2.26739200
C	-6.88445000	2.01287500	-5.53413700	C	8.55204900	-0.19558600	1.06104500
H	-8.65802100	1.74098800	-3.81004300	C	9.93390700	-0.41158900	0.98732700
H	-10.05598300	1.40571900	-2.26765900	H	11.55671500	-1.02897900	-0.31801600
C	-10.48981800	0.85410800	-0.22769900	H	8.08770800	0.14150100	1.97808700
H	-11.55666100	1.02916900	-0.31820400	H	10.55062400	-0.23467300	1.86126400
C	-4.13927100	4.60233900	1.08193800	N	7.72700600	-0.40260200	-0.00141500
C	-0.74287800	-0.01006500	-0.12733600	C	5.73908100	2.07841500	2.02570800
H	-3.76612200	5.59567100	1.30777600	C	5.65407800	2.73338200	3.26774400
H	-0.97929700	2.06136500	0.45570400	C	5.36002900	1.99464500	4.42409800
H	-2.17926300	3.75178900	0.79265100	C	5.81188400	3.80258200	3.33752100
C	-5.36001800	-1.99393000	4.42442600	H	5.24902600	0.00629200	3.05164800
C	-6.59546700	-4.69832100	-0.60706800	C	5.15504900	0.60666200	4.31360900
H	-5.29321800	-2.48922200	5.38738000	H	5.29323100	2.49009600	5.38697100
H	-6.81105600	-5.75768900	-0.69806400	H	5.10229500	-1.05856700	2.92729700
H	-5.81193300	-3.80203600	3.33815500	H	4.92685800	-0.00268500	5.18081200
H	-6.32383700	-4.76582700	1.53238200	N	5.53585000	0.71918700	1.92821800

Table S2. Optimized coordinates for the singlet state of Dp^{4+} .

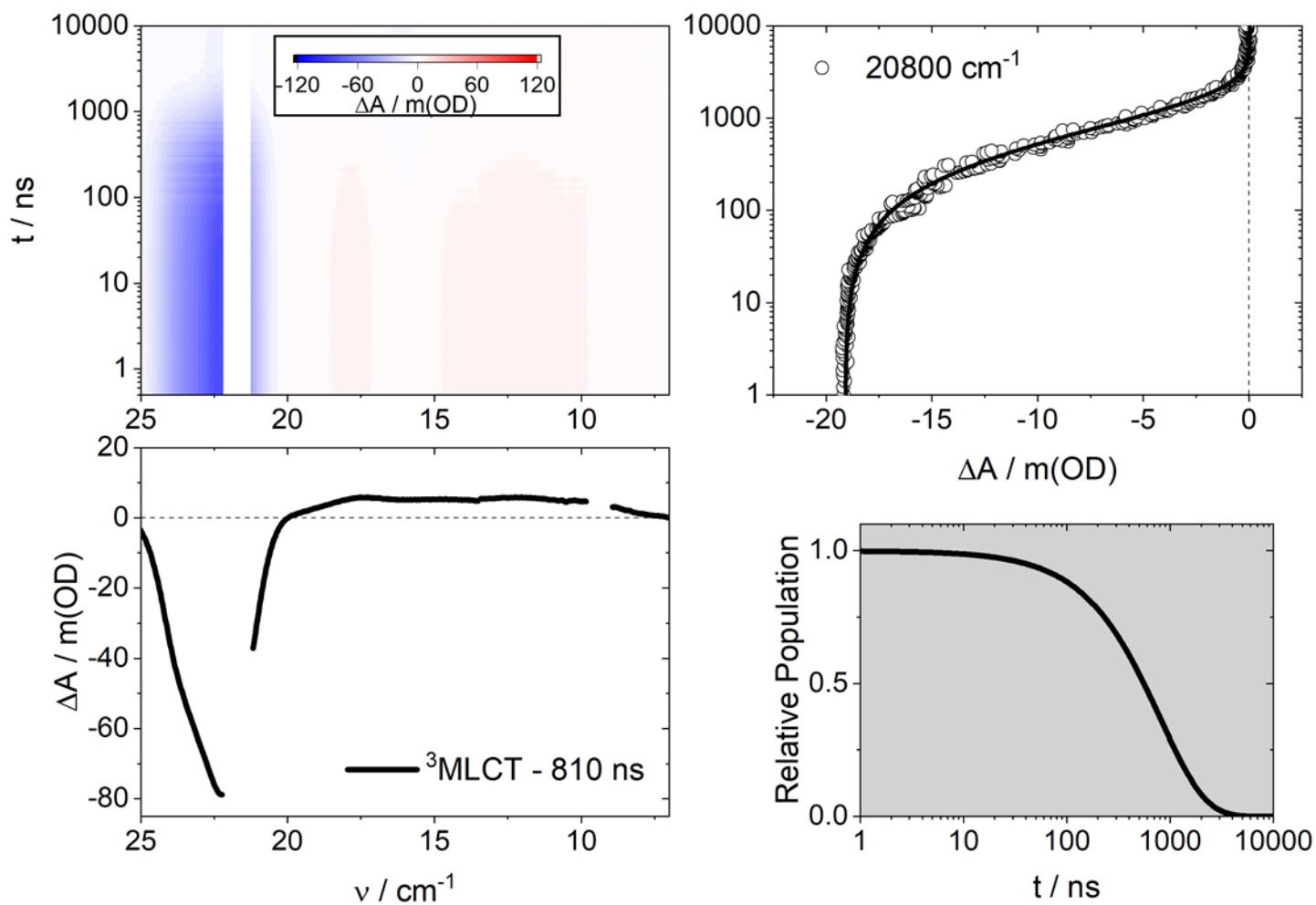


Figure S3. Top left: Differential absorption 3D map obtained upon nsTAS for $[\text{Ru}(\text{bpy})_3]^{2+}$ in ACN upon 460 nm (21700 cm^{-1}) excitation. Top right: Time absorption profile and corresponding fit at 20800 cm^{-1} . Bottom left: Species associated differential spectrum of the $^3\text{MLCT}$ excited state. Bottom right: Concentration evolution over time.

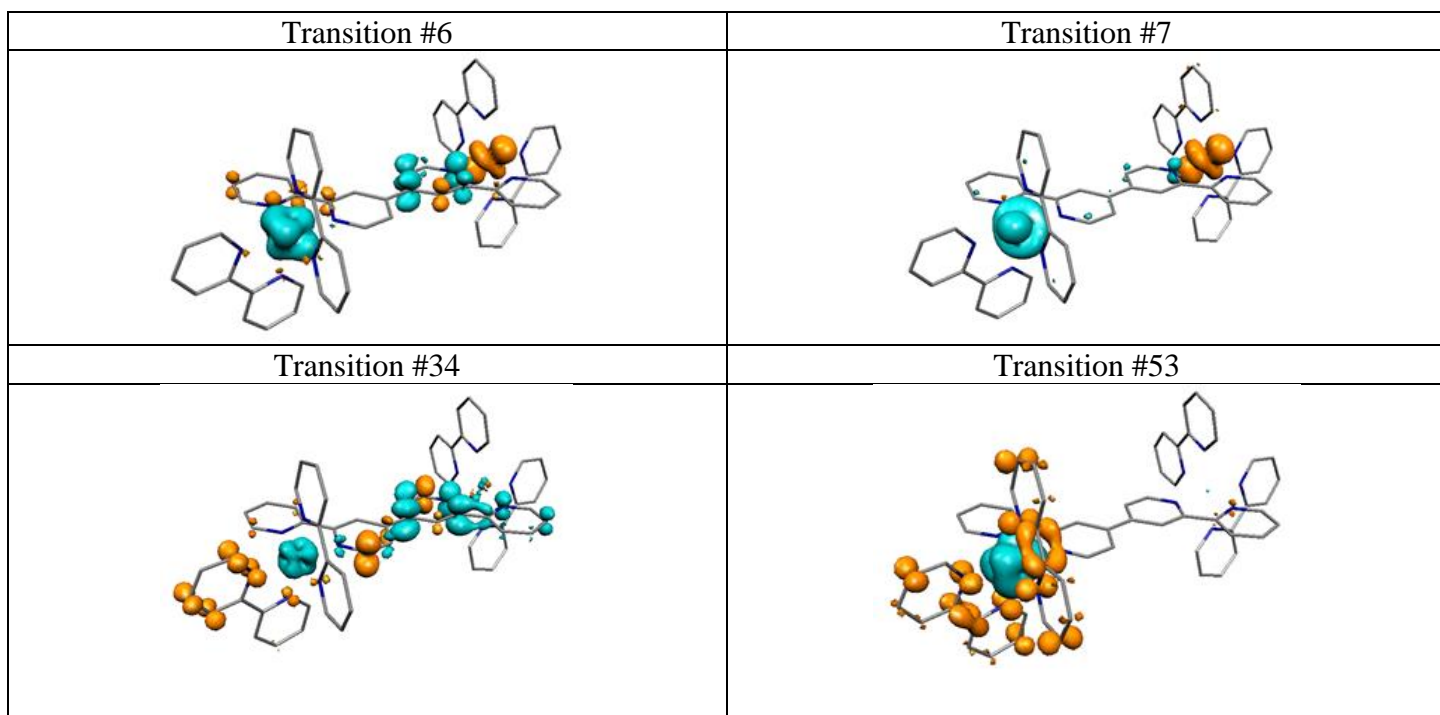


Figure S4. EDDMs (cutoff isovalue = 0.002) for transitions 6, 7, 34 and 53 ($f > 0.1$) for the lowest triplet state of Dp^{4+} . Cyan indicates loss and orange indicates gain of electron density for each transition.

Table S3. Selection ($f > 0.1$) of calculated electronic transitions for the optimized triplet state of Dp^{4+} . Transition #12 is included due to its relevance in the gaussian fitting procedure (*vide infra*).

No.	Energy / cm^{-1}	Osc. Strength	Major contribs	Assignment
6	7185	0.127	HOMO(A)->L+2(A) (48%) H-1(B)->LUMO(B) (21%) HOMO(B)->LUMO(B) (22%)	PIIVCT ($Ru^{II} \rightarrow Ru^{III}$)
7	7904	0.1787	HOMO(A)->L+2(A) (17%) H-1(B)->LUMO(B) (74%)	PIIVCT ($Ru^{II} \rightarrow Ru^{III}$)
12	12304	0.0438	HOMO(A)->L+5(A) (44%), HOMO(A)->L+6(A) (46%)	$\pi^*-\pi^*$ (Lp^+) and LL'CT ($Lp \rightarrow bpy$)
34	19156	0.2301	HOMO(A)->L+15(A) (22%) HOMO(A)->L+18(A) (54%)	MLCT ($Ru^{II} \rightarrow bpy$) LLCT ($Lp \rightarrow bpy$)
53	22672	0.1351	H-3(A)->L+4(A) (27%) H-2(A)->L+3(A) (25%) H-2(B)->L+4(B) (17%)	MLCT ($Ru^{II} \rightarrow bpy$)

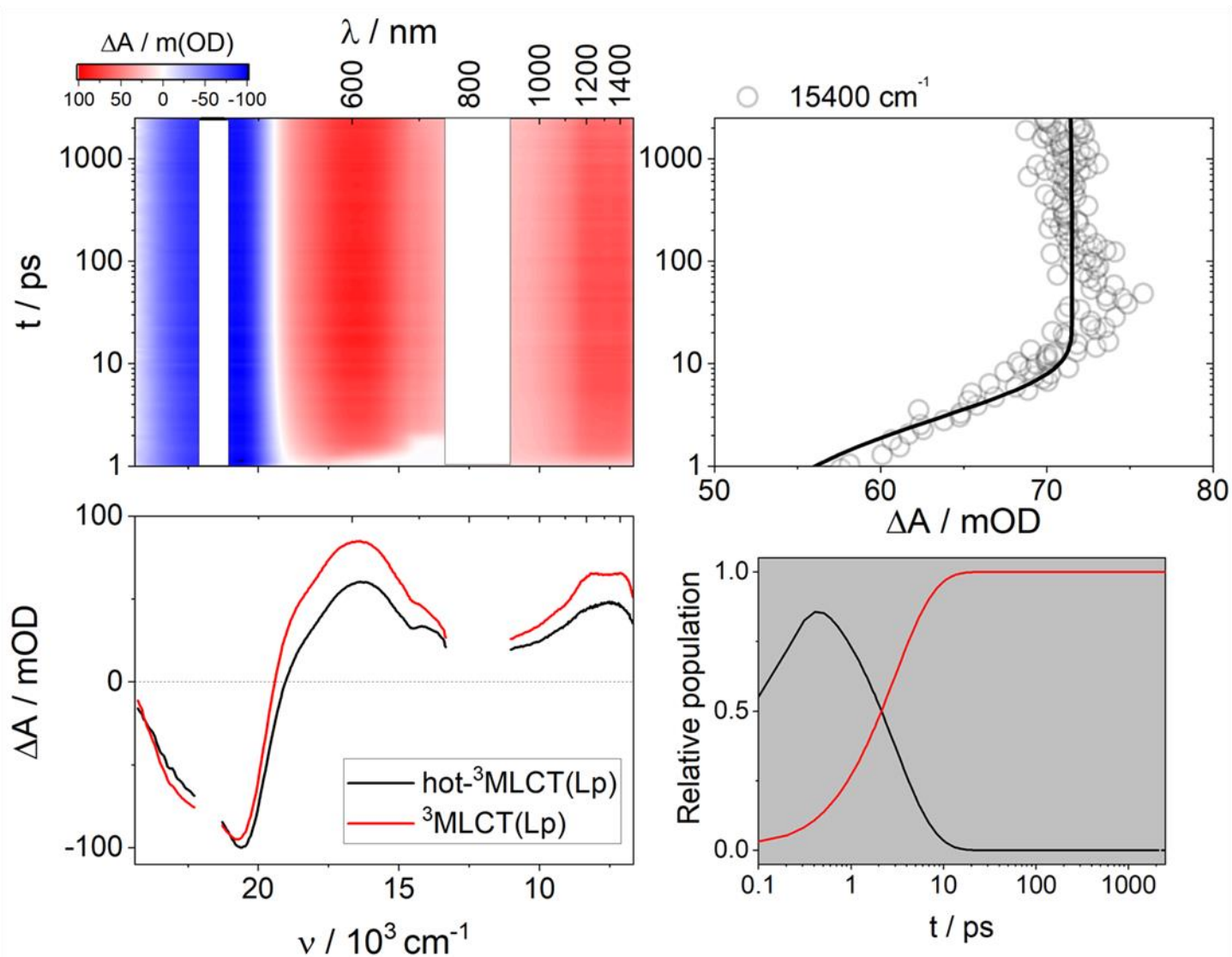


Figure S5. Top left: Differential absorption 3D map obtained upon fsTAS for Dp^{4+} in ACN upon 21700 cm^{-1} excitation. Top right: Time absorption profile and corresponding fit at 15200 and 19500 cm^{-1} . Bottom left: Species associated differential spectrum of the ${}^3\text{MLCT(Lp)}$ excited state. Bottom right: Concentration evolution over time.

Atom	X	Y	Z	C	-0.71679800	0.02580100	0.02268000
Ru	5.65280700	0.07710100	-0.02035200	C	-1.46705200	1.23317600	-0.14711300
C	2.87031900	-1.20383700	0.30197500	C	-1.49506000	-1.15798000	0.18401600
C	8.61645100	0.08810800	-0.94966300	C	-2.85511400	1.21139400	-0.15008000
C	5.20901600	0.02865100	-3.05529800	H	-0.98259100	2.19392900	-0.27017800
C	2.91195400	1.13793700	-0.19627600	C	-2.89194500	-1.12100500	0.17415500
C	8.24191100	0.81968700	1.27114900	H	-1.00473200	-2.11331000	0.31056800
C	5.75159400	-2.05756800	-2.06396900	H	-3.41872200	2.12687100	-0.27462000
C	3.75062800	2.28950800	-0.48367300	N	-3.58418700	0.06461100	0.00967600
C	6.06817400	-2.75311400	-0.80172000	C	-3.74481200	-2.31810500	0.33225500
C	7.22201000	1.07375600	2.30794400	C	-3.25073800	-3.62054600	0.53684000
C	5.99645400	3.05845300	-0.72253800	C	-5.96661000	-3.12795400	0.39962300
C	6.36482600	-2.49968900	1.53311700	C	-4.14457500	-4.69273600	0.67293300
C	4.91052700	0.99790700	2.82358900	H	-2.18419600	-3.80104700	0.59026800
C	1.49400600	-1.21869100	0.29768400	C	-5.52829600	-4.44175100	0.60226700
C	9.99864400	0.27160400	-0.81854900	H	-7.02172500	-2.89557300	0.33740000
C	5.11663700	-0.55562400	-4.32379000	H	-3.77098200	-5.69923500	0.83012000
C	1.51544300	1.15611300	-0.21619800	H	-6.25518500	-5.23998000	0.70202000
C	5.66448900	-2.69302300	-3.31336900	N	-5.10181300	-2.08447100	0.26486600
C	9.62100200	1.01179200	1.46008600	Ru	-5.66388000	-0.08196900	-0.00357700
C	3.27675200	3.59981300	-0.74414500	C	-4.92073800	0.28009200	0.286891800
C	7.50895700	1.58295000	3.58551600	C	-7.21018900	-0.10014700	2.52326900
C	6.35981000	-4.12458900	-0.71030700	C	-5.15645400	0.33782500	4.34827800
C	5.57180500	4.35927700	-0.98872000	H	-3.92558700	0.40926600	2.56423600
C	6.65824900	-3.86136000	1.68197000	C	-7.50348500	-0.05508300	2.96862300
C	5.14349600	1.49636700	4.11144900	C	-6.47049800	0.16527000	4.82251800
H	5.03731100	1.08647900	-2.90859000	H	-4.32838600	0.51172900	5.02624000
H	8.18500200	-0.26830500	-1.87599400	H	-8.51912300	-0.19134700	4.24933000
H	3.42916400	-2.10854600	0.50522400	H	-6.68603400	0.20133700	5.88524600
H	6.35431600	-1.83302600	2.38546700	C	-6.07505600	2.24876400	-1.78225300
H	3.91322200	0.75202100	2.48491000	C	-6.26767100	2.90667100	0.47921900
H	7.04911800	2.80648600	-0.70763900	C	-6.34488900	3.56309300	-2.20575100
H	10.64994100	0.05026900	-1.65592600	C	-6.53677800	4.23159100	0.11377800
H	4.86692900	0.05986500	-5.17998200	H	-6.22609500	2.61201100	1.51956300
H	1.00174900	-2.16055100	0.50407300	C	-6.57816000	4.56632100	-1.25279900
H	6.88276000	-4.25586200	2.66604600	H	-6.37560600	3.80475700	-3.26098700
H	4.30820700	1.64564100	4.78559800	H	-6.71025200	4.97462900	0.88405400
H	6.30323400	5.13543600	-1.18112100	H	-6.78702900	5.58298100	-1.56894600
N	3.61324500	-0.05851600	0.08454500	N	-5.91998800	0.06654500	2.06958500
N	5.52642400	-0.70270700	-1.95324100	N	-6.04033800	1.93054300	-0.44207300
N	7.75802200	0.35904900	0.06916100	C	-8.22299300	-0.32259300	1.47222200
N	5.11630700	2.04282600	-0.48487100	C	-9.59865300	-0.47130300	1.72759400
N	5.92646300	0.78727600	1.94491700	C	-10.48502100	-0.67846200	0.65955700
N	6.07154800	-1.95886600	0.32202900	H	-9.97809300	-0.42367700	2.74082200
C	6.46265600	1.79513500	4.49740500	C	-8.59562000	-0.57456600	-0.84713700
H	6.67410700	2.18654600	5.48672700	C	-9.97332700	-0.73239300	-0.65067600
H	8.52745800	1.81511400	3.87003600	H	-11.54766400	-0.79408700	0.84529000
H	10.00354000	1.36572400	2.40906500	H	-8.16482900	-0.61332400	-1.83899600
C	10.50828000	0.73761900	0.40703800	H	-10.62115600	-0.89141300	-1.50539500
H	11.57462300	0.88380200	0.54176800	N	-7.73230700	-0.37418500	0.18596200
C	4.18090100	4.63157300	-0.99850700	C	-5.81239100	1.12485600	-2.70273200
C	0.74008700	-0.00380300	0.03577100	C	-5.76780100	1.25112100	-4.10346800
H	3.81976400	5.63510800	-1.19909700	C	-5.50810700	0.12177600	-4.89493400
H	1.02567200	2.09341900	-0.44681700	H	-5.93094800	2.21265800	-4.57473300
H	2.21279900	3.80315200	-0.74280100	C	-5.35084500	-1.18697800	-2.86694800
C	5.34767300	-1.93755500	-4.45385300	C	-5.29689000	-1.11902600	-4.26467200
C	6.65573400	-4.68598600	0.54227900	H	-5.47236700	0.20801600	-5.97585900
H	5.28040600	-2.41923600	-5.42346700	H	-5.19702400	-2.12303300	-2.34661400
H	6.88149100	-5.74368300	0.62518300	H	-5.09422000	-2.01731300	-4.83703600
H	5.83754200	-3.75793900	-3.40319800	N	-5.60381200	-0.09435900	-2.09548300
H	6.36008400	-4.74825300	-1.59533700				

Table S4. Optimized coordinates for the triplet state of Dp^{4+} .

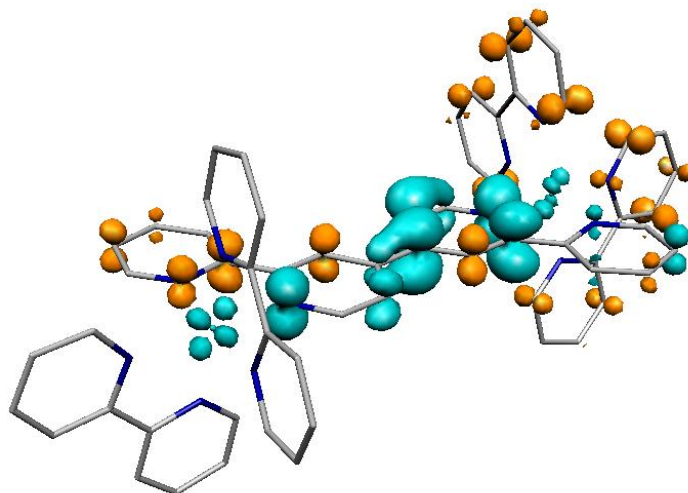


Figure S6. EDDM (cutoff isovalue = 0.002) of the calculated transition #12 for the lowest triplet state of Dp^{4+} .

References

- 1 S. Cerfontaine, L. Troian-Gautier, S. A. M. Wehlin, F. Loiseau, E. Cauët and B. Elias, Tuning the excited-state deactivation pathways of dinuclear ruthenium(II) 2,2'-bipyridine complexes through bridging ligand design, *Dalton Trans.*, 2020, **49**, 8096–8106.
- 2 I. H. M. Van Stokkum, D. S. Larsen and R. Van Grondelle, Global and target analysis of time-resolved spectra, *Biochim. Biophys. Acta - Bioenerg.*, 2004, **1657**, 82–104.
- 3 J. J. Snellenburg, S. Laptanok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, Glotaran: A Java-based graphical user interface for the R package TIMP, *J. Stat. Softw.*, 2012, **49**, 1–22.
- 4 K. M. Mullen and I. H. M. Van Stokkum, TIMP: An R package for modeling multi-way spectroscopic measurements, *J. Stat. Softw.*, 2007, **18**, 1–46.
- 5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, Scuseria, G. E., M. A. Robb, J. R. Cheeseman and D. J. Fox, 2009.
- 6 A. D. Becke, Molecular Bond Energies, *J. Chem. Phys.*, 1986, **84**, 4524.
- 7 A. D. Becke, Thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 8 C. Lee, W. Yang and R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*, 1988, **37**, 785–789.
- 9 J. P. Perdew, Density-functional approximation for the correlation energy of the inhomogeneous electron gas, *Phys. Rev. B*, 1986, **33**, 8822–8824.
- 10 P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.*, 1985, **82**, 270–283.
- 11 P. J. Hay and W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, 1985, **82**, 299–310.
- 12 W. R. Wadt and P. J. Hay, Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, *J. Chem. Phys.*, 1985, **82**, 284–298.
- 13 T. A. Dunning Jr and P. J. Hay, in *Modern theoretical chemistry*, ed. H. F. S. III, Plenum, New York, 1976, p. 1.28.