ELECTRONIC SUPPLEMENTARY INFORMATION

Does Geometry Matter? Effect of Ligand Position in

Bimetallic Ruthenium Polypyridines Siblings

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Structural characterization

Empirical Formula	C50 H45 F12 N11 O P2 Ru2 S
Formula weight	1340.11
Т (К)	100
Crystal system	monoclinic
Space Group	P 2 ₁ /c
a (Å)	13.480(8)
b (Å)	17.680(5)
c (Å)	22.610(4)
α (°)	90
β (°)	92.636(10)
γ (°)	90
V (ų)	5383(4)
Z	4
D _{calc} (mg/m ³)	1.654
Absorption coefficient (mm ⁻¹)	1.071
F (000)	2688.0
λ (Å)	0.82602
heta Range data collection (°)	1.700 / 26.998
Index ranges	-15 ≤ h ≤ 15
	-21 ≤ k ≤ 21
	-28 ≤ l ≤ 27
Reflections collected/unique	112992 / 9893
R _{int}	0.0408
Observed reflections [I>2o(I)]	8792
Completeness (%)	87.3
Maximum / minimum transmission	1.000 / 0.873
Data / restraints / parameters	9893 / 39 / 748
Goodness-of-fit (GOF) on F ²	1.088
Final R-index [I>2 <pre>o</pre> (I)] / all data	0.0508 / 0.573
wR index [I>2σ(I)] / all data	0.1188 / 0.1224
Largest peak and hole (e A ⁻³)	1.280 and -1.444
Weights <i>, w</i>	$1 / [\sigma^2(F_o^2) + (0.0240P)^2]$
	where P = $(F_0^2 + 2F_c^2)^3$

Table S1. Crystallographic data for [RuRuNCS](PF₆)₂.C₃H₆O

bond length, Å				bond length, Å			
Ligand	Ru _{tb} moiety	RuRuNCS	RuRuCl	Ligand	Ru _{py} moiety	RuRuNCS	RuRuCl
CN	Ru1 _{tb} -C(2)	1.981(5)	1.970(12)	NC	Ru _{py} -N(6)	1.997(5)	2.028(10)
	Ru _{tb} -N(7)	2.060(4)	2.087(8)	NCS	Ru _{py} -N(1)	2.077(5)	-
tpy	Ru _{tb} -N(8)	1.949(4)	1.951(8)	py1	Ru _{py} -N(2)	2.071(4)	2.085(11)
	Ru _{tb} -N(11)	2.068(4)	2.082(9)	py2	Ru _{py} -N(3)	2.082(4)	2.102(12)
h m i	Ru _{tb} -N(9)	2.076(4)	2.122(10)	ру3	Ru _{py} -N(4)	2.071(5)	2.098(10)
рру	Ru _{tb} -N(10)	2.074(4)	2.093(9)	py4	Ru _{py} -N(5)	2.089(4)	2.112(13)
	bridge						
CN	C(2)-N(6)	1.173(7)	1.163(14)	NCC	N(1)-C(1)	1.11(1)	
				INCS	C(1)-S(1)	1.653(9)	
angle, degree			angle, degree				
Ru _{tb} (1)-C(2)-N(6)		175.6(5)	176.9(9)	Ru _{py} -N	l(6)-C(2)	179.3(4)	175.2(9)
				N(1)-	-C(1)-S	178.1(7)	

Table S2. Selected Bond Distances and Angles for $[RuRuNCS](PF_6)_2CH_3COCH_3$. and $[RuRuCI](PF_6)_2.CH_3OH$ (extracted from Ref. 1)



Figure S1. 500 MHz ¹H-NMR spectra of complexes **RuRuCl** (Acetone-D₆), **RuRuNO** (Acetone-D₆), **RuRuOH2** (Acetone-D₆), **RuRuDMAP** (Acetone-D₆) and **RuRuACN** (Acetonitrile-D₃), from top to bottom.



Figure S2. Cyclic voltammograms (solid line) and square wave voltammograms (voided circles) for the **RuRuNCS** y **RuRuDMAP** complexes in acetonitrile/0.1 M [TBA]PF₆.



Figure S3. Vis–NIR spectroelectrochemistry for the **RuRuL** complexes in acetonitrile/0.1 M [TBA]PF₆, during the second oxidation processes. The spectra of the [II,III] (red), and [III,III] (blue) species are highlighted.

Solvent dependence of NIR bands



Figure S4. NIR absorption spectra for the **RuRuL** complexes in different solvents: acetonitrile (MeCN), dichloromethane (DCM) and nitromethane (NM).



Figure S5. IR spectroelectrochemistry for the **RuRuL** complexes in acetonitrile/0.1 M [TBA]PF₆, during the second oxidation processes. The spectra of the [II,III] (red), and [III,III] (blue) species are highlighted.

DFT Calculations



Figure S6. Comparison of the experimental vis-NIR spectra of the **RuRuL** complexes species in acetonitrile/0.1 M $[TBA]PF_6$ and the energy of the transitions calculated by (TD)DFT calculations (bars).



Figure S7. Comparison of the experimental vis-NIR spectra of the **RuRuL** complexes species in acetonitrile/0.1 M $[TBA]PF_6$ and the energy of the transitions calculated by (TD)DFT calculations (bars).

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
20	23285	0.1101	$H-3 \rightarrow L+1 (23\%)$	$d\pi_{xy}(Ru_{pp}), d\pi_{xz}(Ru_{py}) \rightarrow \pi^{*}(tpy, bpy)$
			H-3 → L+2 (49%)	
			HOMO \rightarrow L+2 (12%)	
76	28580	0.1336	H-2 → L+6 (24%)	$d\pi_{xy}(Ru_{py}), d\pi_{xz}(Ru_{py}, Ru_{pp}) \rightarrow \pi^{*}(py, tpy)$
			HOMO → L+7 (37%)	
			HOMO $ ightarrow$ L+8 (11%)	
77	28632	0.1516	H-2 → L+5 (37%)	$d\pi_{xy}(Ru_{py}), d\pi_{xz}(Ru_{pp}) \rightarrow \pi^{*}(py)$
			H-2 → L+6 (17%)	
			HOMO \rightarrow L+8 (21%)	
78	28687	0.1359	H-2 → L+5 (21%)	$d\pi_{xy}(Ru_{py}), d\pi_{xz}(Ru_{pp}) \rightarrow \pi^{*}(py, tpy)$
			H-2 → L+6 (15%)	
			HOMO \rightarrow L+8 (16%)	

Table S3-A. Selected electronic transitions (f > 0.05) for the singlet **RuRuACN**³⁺ ion calculated in MeCN



Figure S8-A. Electron density difference maps of the selected energy electronic transitions for the singlet **RuRuACN³⁺** ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

Table S3-B. Selected electronic transitions (f > 0.05) for the singlet **RuRuDMAP**³⁺ ion calculated in MeCN.

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
25	22612	0.0885	$H-3 \rightarrow L+1 (33\%)$	$d\pi_{xy}(Ru_{pp}) \rightarrow \pi^*(tpy, bpy)$
			$H-3 \rightarrow L+2 (40\%)$	
71	26976	0.1135	H-2 → L+4 (39%)	dπ _{xy} (Ru _{py}) → π*(py)
			H-2 → L+5 (28%)	
			H-2 → L+6 (11%)	
72	27100	0.0787	H-2 → L+4 (20%)	$d\pi_{xy}(Ru_{py}) \rightarrow \pi^*(py)$
			H-2 → L+5 (36%)	
			H-2 → L+7 (21%)	
77	27323	0.1216	H-6 → LUMO (15%)	$d\pi_{xy}(Ru_{py}) \rightarrow \pi^*(py)$
			H-2 → L+3 (12%)	
			H-2 → L+5 (11%)	
			$H-2 \rightarrow L+6 (16\%)$	
			H-2 → L+7 (18%)	
106	29511	0.1148	H-2 → L+22 (13%)	$d\pi_{xy}(Ru_{py}, Ru_{py}) \rightarrow \pi^*(bpy, py)$
			$H-1 \rightarrow L+10 (24\%)$, , , , , , , , , , , , , , , , , , , ,
			HOMO \rightarrow L+12 (18%)	



Figure S8-B. Electron density difference maps of the selected energy electronic transitions for the singlet **RuRuDMAP³⁺** ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

Table S3-C. Selected electronic transitions (f > 0.05) for the singlet **RuRuNCS**²⁺ ion calculated in MeCN.

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
37	23345	0.0828	H-4 → L+1 (78%)	$d\pi_{xy}(Ru_{pp}) \rightarrow \pi^*(tpy, bpy)$
79	27114	0.1611	H-2 → L+6 (46%)	$d\pi_{xy}(Ru_{py}) \rightarrow \pi^*(py)$
			H-2 → L+7 (17%)	
80	27132	0.1840	H-2 → L+6 (28%)	$d\pi_{xy}(Ru_{py}) \rightarrow \pi^*(py)$
			$H-2 \rightarrow L+7 (43\%)$	



Figure S8-C. Electron density difference maps of the selected energy electronic transitions for the singlet **RuRuNCS**²⁺ ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

Table S3-D. Selected electronic transitions (f > 0.05) for the singlet **RuRuCl**²⁺ ion calculated in MeCN.

No.	Energy (cm⁻¹)	Osc. Strength	Major contribs	Assignment
31	22144	0.0639	H-3 → L+1 (63%) H-3 → L+2 (23%)	$d\pi_{xy}(Ru_{pp}) ightarrow \pi^*(tpy, bpy)$
39	23649	0.0631	H-4 → L+1 (90%)	$d\pi_{yz}(Ru_{pp}) \rightarrow \pi^*(tpy, bpy)$
77	26596	0.2056	H-2 → L+6 (14%) H-2 → L+7 (32%) H-2 → L+8 (15%)	$d\pi_{xy}(Ru_{py}) \rightarrow \pi^*(py)$
78	26648	0.2236	H-2 → L+6 (32%) H-2 → L+7 (20%) H-2 → L+9 (15%)	$d\pi_{xy}(Ru_{py}) ightarrow \pi^*(py)$



Figure S8-D. Electron density difference maps of the selected energy electronic transitions for the singlet **RuRuCl**²⁺ ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

Table S4-A. Selected electronic transitions for the doublet RuRuACN⁴⁺ ion calculated in MeCN.

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
1	932	0.0000	H-1β → LUMOβ (100%)	$d\pi_{xz}(Ru_{pp},Ru_{py}) \rightarrow d\pi_{yz}(Ru_{pp},Ru_{py})$
2	3147	0.0002	H-2β → LUMOβ (98%)	$d\pi_{xy}(Ru_{py}) \rightarrow d\pi_{yz}(Ru_{pp},Ru_{py})$
3	3655	0.0185	H-3β → LUMOβ (64%)	$d\pi_{xy}(Ru_{pp}) \rightarrow d\pi_{yz}(Ru_{pp},Ru_{py})$
			HOMO $\beta \rightarrow$ LUMO β (34%)	
4	6932	0.2353	H-3β → LUMOβ (33%)	$d\pi_{xy}(Ru_{py}) \rightarrow d\pi_{yz}(Ru_{pp},Ru_{py})$
			HOMOβ → LUMOβ (64%)	
5	7411	0.0005	H-4β → LUMOβ (96%)	$d\pi_{xz}(Ru_{pp},Ru_{py}) \rightarrow d\pi_{yz}(Ru_{pp},Ru_{py})$
6	14950	0.0050	H-5β → LUMOβ (91%)	$\pi(tpy) \rightarrow d\pi_{yz}(Ru_{pp}, Ru_{py})$
7	15629	0.0009	H-6β → LUMOβ (92%)	$\pi(bpy) \rightarrow d\pi_{yz}(Ru_{pp}, Ru_{py})$



Electronic Transition #1 932 cm⁻¹ *f*=0.0000



Electronic Transition #4 6932 cm⁻¹ *f*=0.2352



Electronic Transition #2 3147 cm⁻¹ *f*=0.0002

Electronic Transition #3 3655 cm⁻¹ *f*=0.0185



Electronic Transition #6 14950 cm⁻¹ *f*=0.0050





Electronic Transition #7 15629 cm⁻¹ *f*=0.0009

Figure S9-A. Electron density difference maps of the lowest energy electronic transitions for doublet **RuRuACN**⁴⁺ ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

 Table S4-B. Selected electronic transitions for the doublet RuRuDMAP⁴⁺ ion calculated in MeCN.

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
1	2099	0.0006	H-5β → LUMOβ (40%) H-2β → LUMOβ (30%) HOMOβ → LUMOβ (21%)	$d\pi_{xz}(Ru_{pp},Ru_{py}) \rightarrow d\pi_{yz}(Ru_{py})$
2	3735	0.0004	H-4β → LUMOβ (96%)	$d\pi_{xy}(Ru_{py}) \rightarrow d\pi_{yz}(Ru_{pp},Ru_{py})$
3	6642	0.0236	H-1β → LUMOβ (53%) HOMOβ → LUMOβ (42%)	$d\pi_{xy}(Ru_{pp}), d\pi y_z(Ru_{pp}) \rightarrow d\pi_{yz}(Ru_{py})$
4	7907	0.1896	H-2β → LUMOβ (11%) H-1β → LUMOβ (42%) HOMOβ → LUMOβ (34%)	$d\pi_{xy}(Ru_{pp}), d\pi_{yz}(Ru_{pp}) \rightarrow d\pi_{yz}(Ru_{py})$
5	8990	0.0745	H-5β → LUMOβ (38%) H-2β → LUMOβ (57%)	$d\pi_{xz}(Ru_{pp},Ru_{py}) \rightarrow d\pi_{yz}(Ru_{py},Ru_{pp})$
6	11108	0.0959	H-3β → LUMOβ (91%)	$\pi(\text{DMAP}) \rightarrow d\pi_{yz}(\text{Ru}_{py})$



Electronic Transition #4 7907 cm⁻¹ *f*=0.1896 Electronic Transition #5 8990 cm⁻¹ *f*=0.0745 Electronic Transition #6 11108 cm⁻¹ *f*=0.0959

Figure S9-B. Electron density difference maps of the lowest energy electronic transitions for doublet **RuRuDMAP**⁴⁺ ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

Table S4-C. Selected electronic transitions for the doublet RuRuNCS³⁺ ion calculated in MeCN.

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
1	592	0.0000	H-8β → LUMOβ (10%) H-1β → LUMOβ (12%) HOMOβ → LUMOβ (71%)	$d\pi_{xz}(Ru_{pp},Ru_{py}) \rightarrow d\pi_{yz}(Ru_{py},Ru_{pp})$
2	3751	0.0004	H-5β → LUMOβ (20%) H-4β → LUMOβ (76%)	$d\pi_{xy}(Ru_{py}) \rightarrow d\pi_{yz}(Ru_{py},Ru_{pp})$
3	7641	0.0349	H-2 β → LUMO β (27%) H-1 β → LUMO β (60%) HOMO β → LUMO β (11%)	$d\pi_{xy}(Ru_{pp}) \rightarrow d\pi_{yz}(Ru_{py})$
4	8794	0.1190	H-3β → LUMOβ (16%) H-2β → LUMOβ (63%) H-1β → LUMOβ (11%)	$d\pi_{xy}(Ru_{pp}) \rightarrow d\pi_{yz}(Ru_{py})$
5	9421	0.0655	H-3β → LUMOβ (75%) H-1β → LUMOβ (13%)	$d\pi_{xz}(Ru_{pp}) \rightarrow d\pi_{yz}(Ru_{py})$
6	13157	0.0000	H-8β → LUMOβ (85%)	$\pi(NCS) \rightarrow d\pi_{yz}(Ru_{py}, Ru_{pp})$
7	13774	0.1148	H-5β → LUMOβ (76%) H-4β → LUMOβ (20%)	$\pi(NCS) \rightarrow d\pi_{yz}(Ru_{py}, Ru_{pp})$





Electronic Transition #2 3751 cm⁻¹ *f*=0.0004



Electronic Transition #3 7641 cm⁻¹ *f*=0.0349



Electronic Transition #1 592 cm⁻¹ *f*=0.0000

Electronic Transition #4 8794 cm⁻¹ *f*=0.1190



Electronic Transition #5 9421 cm⁻¹ *f*=0.0655



Electronic Transition #6 13157 cm⁻¹ *f*=0.0000



Electronic Transition #7 13774 cm⁻¹ *f*=0.1148

Figure S9-C. Electron density difference maps of the lowest energy electronic transitions for doublet **RuRuNCS**³⁺ ion. Purple indicates a decrease in charge density, while cyan indicates an increase.

 Table S4-D. Selected electronic transitions for the doublet RuRuCl³⁺ ion calculated in MeCN.

No.	Energy (cm ⁻¹)	Osc. Strength	Major contribs	Assignment
1	771	0.0000	H-3β → LUMOβ (33%)	$d\pi_{yz}(Ru_{pp},Ru_{py}) \rightarrow d\pi_{xz}(Ru_{py})$
			H-1β → LUMOβ (10%)	
			HOMOβ → LUMOβ (44%)	
2	2622	0.0004	H-4β → LUMOβ (97%)	$d\pi_{xy}(Ru_{py}) \rightarrow d\pi_{xz}(Ru_{py},Ru_{pp})$
3	7998	0.0116	H-1 $\beta \rightarrow$ LUMO β (68%)	$d\pi_{xy}(Ru_{pp}) \rightarrow d\pi_{xz}(Ru_{py})$
			HOMOβ → LUMOβ (28%)	
4	9382	0.0761	H-3β → LUMOβ (20%)	$d\pi_{xz}(Ru_{pp}), d\pi_{yz}(Ru_{pp}) \rightarrow d\pi_{xz}(Ru_{py})$
			H-2β → LUMOβ (39%)	
			H-1β → LUMOβ (14%)	
			HOMOβ → LUMOβ (24%)	
5	10291	0.0681	H-3β → LUMOβ (38%)	$d\pi_{xz}(Ru_{pp}) \rightarrow d\pi_{xz}(Ru_{py})$
			H-2β \rightarrow LUMOβ (50%)	
6	18374	0.0021	H-5β → LUMOβ (67%)	$\pi(tpy) \rightarrow d\pi_{xz}(Ru_{py}, Ru_{pp})$
8	18994	0.0105	H-7β \rightarrow LUMOβ (80%)	$\pi(CI) \rightarrow d\pi_{xz}(Ru_{py}, Ru_{pp})$



Electronic Transition #2 2622 cm⁻¹ *f*=0.0004







Electronic Transition #1 771 cm⁻¹ *f*=0.0000



Electronic Transition #4 9382 cm⁻¹ *f*=0.0761



Electronic Transition #5 10291 cm⁻¹ *f*=0.0681



Electronic Transition #6 18374 cm⁻¹ *f*=0.0021



Electronic Transition #39 18994 cm⁻¹ *f*=0.0105

Figure S9-D. Electron density difference maps of the lowest energy electronic transitions for doublet **RuRuCl³⁺** ion. Purple indicates a decrease in charge density, while cyan indicates an increase.



H-4β (-7.63 eV) 43% Ru_{pp}, 26% Ru_{py}

H-5β (-7.79 eV) 19% bpy, 78% tpy

H-6β (-7.83 eV) 81% bpy, 18% tpy









L+1β (-3.05 eV) 5% Ru_{pp}, 0% Ru_{py}, 93% tpy

LUMOβ (-5.02 eV) 9% Ru_{pp}, 60% Ru_{py}, 19% DMAP

HOMOβ (-6.45 eV) 63% Ru_{pp}, 4% Ru_{py}, 10% DMAP



H-1β (-6.61 eV) 73% Ru_{pp}, 1% Ru_{py}, 3% DMAP





H-2β (-6.64 eV) 58% Ru_{pp}, 7% Ru_{py}, 11% DMAP

H-3β (-7.00 eV) 9% Ru_{pp}, 18% Ru_{py}, 63% DMAP



H-4β (-7.42 eV) 0% Ru_{pp}, 79% Ru_{py}, 20% py





H-6β (-7.61 eV) 13% bpy, 80% tpy, 0% DMAP

H-5β (-7.48 eV) 8% Ru_{pp}, 63% Ru_{py}, 11% tpy

Figure S10-B. Computed β -orbitals for the doublet RuRuDMAP⁴⁺ ion calculated in MeCN.







L+1β (-3.00 eV) 1% Ru_{pp}, 5% Ru_{py}, 93% tpy

LUMOβ (-4.85 eV) 7% Ru_{pp}, 52% Ru_{py}, 22% NCS

HOMOβ (-6.34 eV) 36% Ru_{pp}, 23% Ru_{py}, 24% NCS







H-1β (-6.44 eV) 59% Ru_{pp}, 7% Ru_{py}, 14% NCS

H-2β (-6.56 eV) 71% Ru_{pp}, 1% Ru_{py}, 4% NCS

H-3β (-6.82 eV) 41% Ru_{pp}, 5% Ru_{py}, 37% NCS



H-4β (-7.20 eV) 1% Ru_{pp}, 65% Ru_{py}, 15% NCS



H-5β (-7.21 eV) 3% Ru_{pp}, 31% Ru_{py}, 54% NCS



H-8β (-7.75 eV) 4% Ru_{pp}, 41% Ru_{py}, 34% NCS

Figure S10-C. Computed β -orbitals for the doublet RuRuNCS³⁺ ion calculated in MeCN.







L+1β (-3.02 eV) 5% Ru_{pp}, 0% Ru_{py}, 93% tpy



H-1β (-6.56 eV) 72% Ru_{pp}, 4% Ru_{py}, 1% CI







HOMOβ (-6.42 eV) 59% Ru_{pp}, 14% Ru_{py}, 3% CI

H-2β (-6.67 eV) 62% Ru_{pp}, 9% Ru_{py}, 3% Cl

H-3β (-7.18 eV) 18% Ru_{pp}, 41% Ru_{py}, 21% CI



Figure S10-D. Computed β -orbitals for the doublet RuRuCl³⁺ ion calculated in MeCN.



Figure S11. Comparison of the experimental IR spectra of the **RuRuL** complexes species in acetonitrile/0.1 M [TBA]PF₆ and the energy of the cyanide stretch calculated by (TD)DFT calculations (bars).



Figure S12. Comparison of the experimental IR spectra of the **RuRuL** complexes species in acetonitrile/0.1 M [TBA] PF_6 and the energy of the cyanide stretch calculated by (TD)DFT calculations (bars).



Figure S13. Computed spin density and Mulliken spin densities for the RuRuL (III,III) species.

Comparison between Ruthenium Polypyridines Siblings

[Ru(tpy)(bpy)(μ-CN)Ru(bpy)₂L)] ^{4/3+} *			[Ru(tpy)(bpy)	(μ-CN)Ru(py)₄L)] ^{4/3+}
L	Δ <i>Ε</i> / V	$v_{max} / 10^3 \text{ cm}^{-1}$	ΔΕ / V	$v_{max} / 10^3 \text{ cm}^{-1}$
	0.92		0.07	
Ci	0.83	10.8 (2.6)	0.87	10.4 (3.9)
SCN ⁻	0.63	9.5 (3.2)	0.75	9.7 (4.3)
DMAP	0.58	8.4 (4.0)	0.61	8.9 (7.5)
ACN	0.53	6.9 (9.3)	0.44	6.8 (9.5)

Table S5. Energy and molar absorptivity of the IVCT transition the family of complexes $[Ru(tpy)(bpy)(\mu-CN)Ru(bpy)_2L)]^{4/3+}$ and $[Ru(tpy)(bpy)(\mu-CN)Ru(py)_4L)]^{4/3+}$.

* Data extracted from Ref²



Figure S14. Dependence of the molar absorptivity of the IVCT transition with $\Delta E_{\frac{1}{2}}$ between the two redox couples for the family of complexes $[Ru(tpy)(bpy)(\mu-CN)Ru(bpy)_2L)]^{4/3+}$ (blue) and $[Ru(tpy)(bpy)(\mu-CN)Ru(py)_4L)]^{4/3+}$ (red).

References

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