Supplementation information for the manuscript:

Comparative photo-release of nitric oxide from isomers of substituted terpyridinenitrosylruthenium(II) complexes: experimental and computational investigations.

by Joëlle Akl, Isabelle Sasaki, Pascal G. Lacroix, Isabelle Malfant, Sonia Mallet-Ladeira, Patricia Vicendo, Norberto Farfán, and Rosa Santillan.

S1. ^{1}H-NMR spectrum of the mixture of isomers.

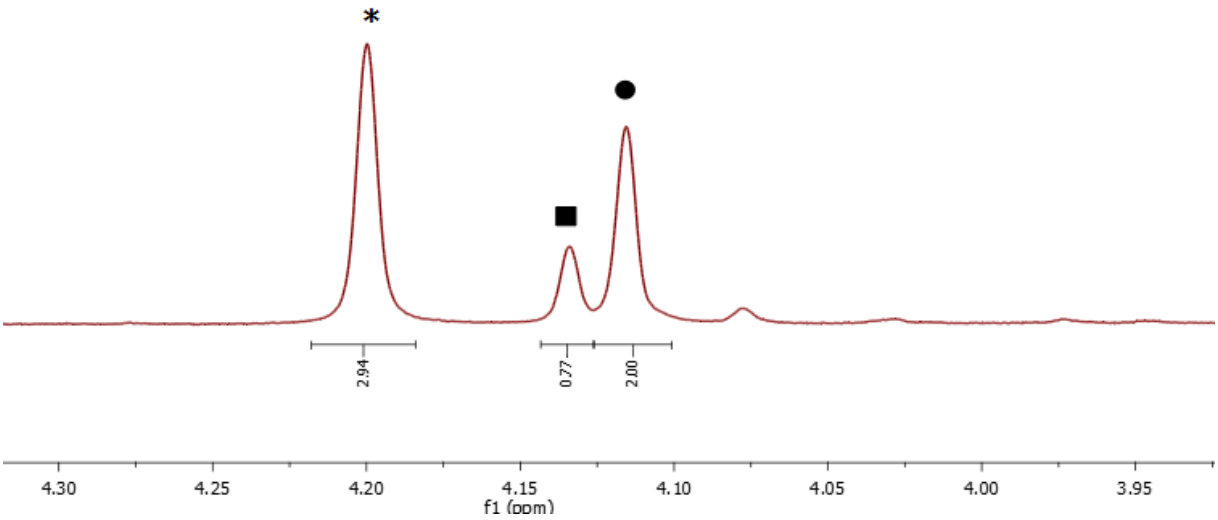
S2. Comparison of the B3PW91 computed coordination sphere around ruthenium(II) versus the experimental (X-ray) observations.

S3. Computed coordinates for FT, *trans*(Cl-Cl)-[Ru^{II}(FT)Cl_2(NO)]$^+$, *cis*(Cl-Cl)-[Ru^{II}(FT)Cl_2(NO)]$^+$, and *trans*(Cl-Cl)-[Ru(terpyridine)Cl_2(NO)]+.

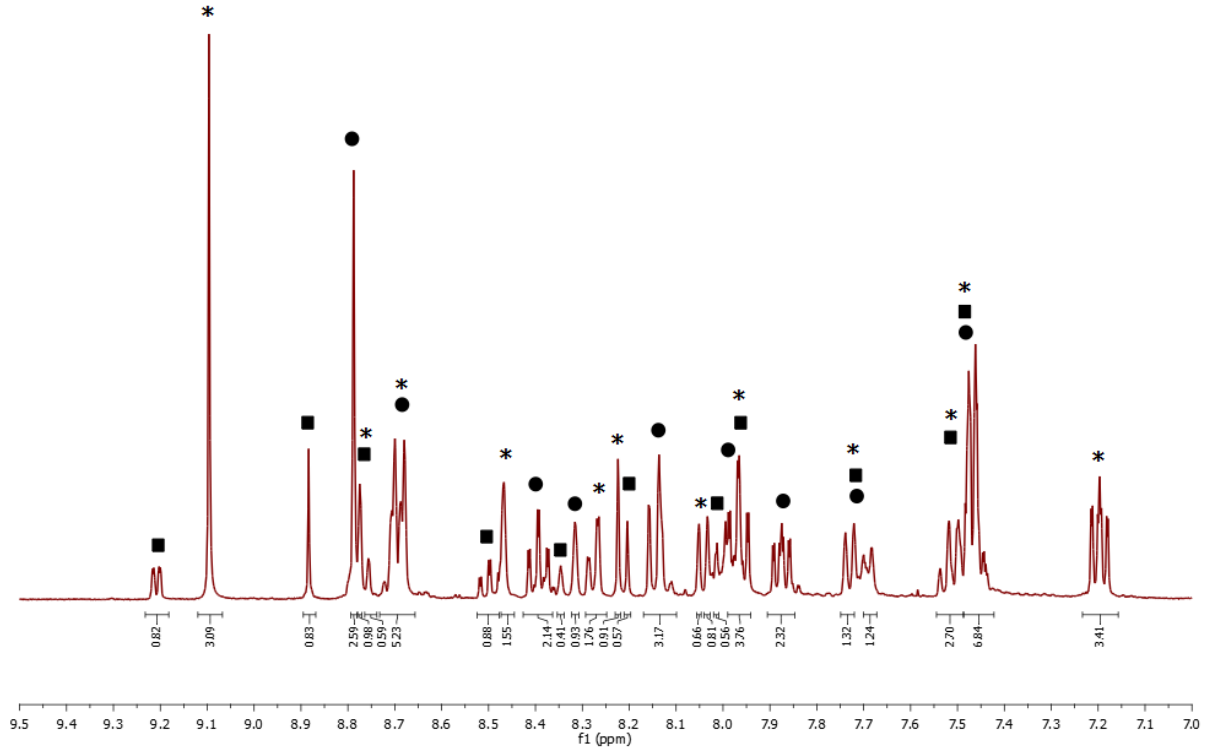
S4. CAM-B3LYP computed DFT spectra for FT, *trans*(Cl-Cl)-[Ru^{II}(FT)Cl_2(NO)]$^+$, and *cis*(Cl-Cl)-[Ru^{II}(FT)Cl_2(NO)]$^+$.

S5. Voltamogram of *trans*(Cl-Cl)-[Ru(FT)Cl_2(NO)](PF_6)

S1. ^{1}H-NMR spectrum of the mixture of isomers: $[Ru^{II}(FT)_2](PF_6)_2$ (star), *cis*(Cl,Cl)-$[Ru^{II}(FT)Cl_2(NO)](PF_6)$ (square), and *trans*(Cl,Cl)-$[Ru^{II}(FT)Cl_2(NO)](PF_6)$ (circle).

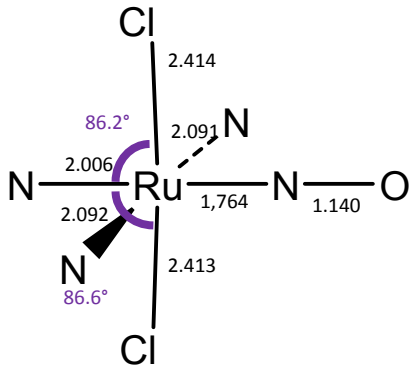


a) aliphatic part

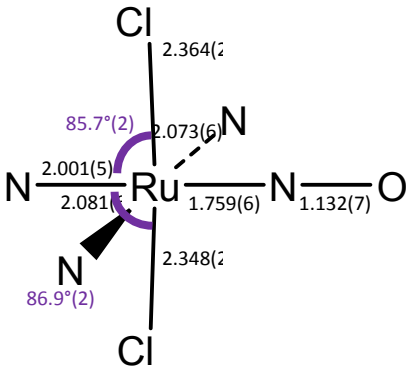


b) aromatic part

S2. Comparison of the B3PW91 computed coordination sphere around ruthenium(II) versus the experimental (X-ray) observations.



B3PW91/6-31G*



X-ray diffraction

S3. Computed coordinates for FT, *trans*(Cl-Cl)-[Ru^{II}(FT)$(Cl)_2$(NO)]$^+$, and *cis*(Cl-Cl)-[Ru^{II}(FT)$(Cl)_2$(NO)]$^+$, and *trans*(Cl-Cl)-[Ru(terpyridine)(Cl)2(NO)]$^+$.

4'-(2-fluorenyl)-2,2':6',2''-terpyridine (FT).

C	5.309320	4.225973	-1.073974
C	5.443412	5.035214	-2.317517
C	6.363133	6.088061	-2.394584
H	6.986508	6.316150	-1.537793
C	6.452163	6.817349	-3.575274
H	7.157600	7.639604	-3.660279
C	5.624742	6.476578	-4.642792
H	5.659429	7.017124	-5.583663
C	4.740703	5.411912	-4.471484
H	4.077026	5.113982	-5.282130
C	6.023110	3.827631	1.076603
C	6.932708	4.206357	2.193781
C	7.844830	5.259232	2.053392
H	7.889049	5.805344	1.118213
C	8.674200	5.576487	3.123598
H	9.390851	6.389167	3.040268

C	8.570513	4.837374	4.299796
H	9.196701	5.049259	5.160987
C	7.632263	3.806815	4.344564
H	7.520502	3.205264	5.245680
C	5.116443	2.775106	1.229942
H	5.074917	2.256732	2.180829
C	4.267230	2.434776	0.171038
C	4.378083	3.185961	-1.004448
H	3.772108	2.968516	-1.876306
C	3.291183	1.328603	0.290390
C	3.599564	0.183662	1.047288
H	4.573056	0.106399	1.523897
C	2.696627	-0.867733	1.174033
H	2.964713	-1.744823	1.757420
C	1.457235	-0.776413	0.538347
C	1.136177	0.365511	-0.222600
C	2.041279	1.407566	-0.349765
H	1.778583	2.295428	-0.919771
C	-0.253416	0.231439	-0.797499
H	-0.250324	0.276664	-1.895038
H	-0.917344	1.038462	-0.458918
C	-0.696818	-1.118582	-0.286772
C	-1.897158	-1.789070	-0.489602
H	-2.686316	-1.347151	-1.093575
C	-2.078341	-3.045145	0.096694
H	-3.012893	-3.579492	-0.053856
C	-1.069120	-3.621365	0.875553
H	-1.227398	-4.598958	1.323714
C	0.138034	-2.954273	1.082513
H	0.918457	-3.407630	1.688744
C	0.320470	-1.699379	0.497593
N	6.117459	4.541260	-0.053137
N	4.643395	4.703944	-3.344964
N	6.830497	3.490644	3.326302

Cis(Cl-Cl)-[Ru(FT)(Cl)2(NO)]+

Ru	3.282505	0.085596	0.129296
Cl	3.230864	-0.075721	-2.233746
N	1.307007	-0.049591	0.045240
C	0.600261	1.087622	-0.084774
C	1.435683	2.303225	-0.178208
N	3.052052	-1.991942	0.159856
C	-2.892350	-0.333603	-0.153958
C	-7.131833	-0.391527	-0.170568
N	2.784415	2.101735	-0.115881

C	3.172135	4.436322	-0.381110
H	3.886895	5.247759	-0.458252
C	0.754558	-1.276135	0.065596
C	-0.627486	-1.393277	0.003086
H	-1.095426	-2.368647	0.055478
C	3.743933	-4.269750	0.220802
H	4.558865	-4.984015	0.251443
C	1.741596	-2.373978	0.138189
C	-1.424764	-0.236934	-0.097596
C	0.923977	3.585457	-0.341664
H	-0.146517	3.745933	-0.392909
C	-0.784210	1.015913	-0.153498
H	-1.370635	1.917012	-0.283435
C	3.628902	3.132198	-0.215213
H	4.683890	2.886995	-0.160869
C	4.024943	-2.906820	0.197544
H	5.038039	-2.519891	0.207189
C	1.403690	-3.722192	0.160691
H	0.364177	-4.027347	0.142025
C	2.415782	-4.679400	0.203827
H	2.161944	-5.734244	0.221726
C	1.802059	4.662984	-0.443702
H	1.412583	5.667566	-0.572101
C	-7.411067	0.799534	0.530580
C	-9.761316	0.367642	0.299951
H	-10.794083	0.655185	0.479074
C	-8.167437	-1.204848	-0.637760
H	-7.957315	-2.123864	-1.179062
C	-9.483784	-0.814788	-0.396235
H	-10.302906	-1.434256	-0.751822
C	-8.726282	1.182569	0.767342
H	-8.950957	2.099254	1.307261
Cl	5.722688	0.236495	0.007136
C	-3.692655	0.672679	0.422045
H	-3.232880	1.511175	0.938775
C	-4.894570	-1.538574	-0.849339
H	-5.347991	-2.387640	-1.352985
C	-5.071379	0.562455	0.367892
C	-3.510263	-1.431937	-0.782895
H	-2.900085	-2.194327	-1.258810
C	-5.679990	-0.540062	-0.268313
C	-6.126164	1.487425	0.923726
H	-6.051074	2.497473	0.498789
H	-6.035983	1.603082	2.012278
N	3.465898	0.213827	1.870307
O	3.700177	0.304006	2.983033

Trans(Cl-Cl)-[Ru(FT)(Cl)2(NO)]+

Ru	3.365748	0.086672	0.035375
Cl	3.334286	-0.087398	-2.370827
Cl	3.095556	0.242309	2.429287
N	1.366078	-0.048902	-0.048739
C	0.645976	1.083786	-0.145404
C	1.469560	2.302251	-0.199593
N	3.078585	-1.981095	0.158079
C	-2.850419	-0.329820	-0.187741
C	-7.089361	-0.396387	-0.183353
N	2.814917	2.098305	-0.129500
C	3.185080	4.452047	-0.286006
H	3.898553	5.267697	-0.316021
C	0.798039	-1.267977	0.002825
C	-0.583642	-1.385832	-0.041595
H	-1.049614	-2.360479	0.032741
C	3.751797	-4.265162	0.333840
H	4.564544	-4.977569	0.417936
C	1.771923	-2.365353	0.118803
C	-1.383414	-0.232398	-0.141494
C	0.949130	3.586673	-0.315735
H	-0.122293	3.737729	-0.372441
C	-0.738860	1.017158	-0.193820
H	-1.322989	1.922630	-0.299766
C	3.647970	3.145903	-0.171548
H	4.707793	2.933272	-0.113422
C	4.040494	-2.906817	0.262870
H	5.062730	-2.551564	0.289826
C	1.423961	-3.710145	0.184167
H	0.382431	-4.006489	0.149274
C	2.423858	-4.672383	0.293258
H	2.163321	-5.724315	0.344731
C	1.815431	4.675429	-0.359441
H	1.420290	5.681775	-0.449711
C	-7.367695	0.796057	0.515877
C	-9.718032	0.358464	0.297527
H	-10.750546	0.644273	0.480823
C	-8.125406	-1.213206	-0.643540
H	-7.915856	-2.133226	-1.183347
C	-9.441365	-0.825243	-0.396898
H	-10.260870	-1.447327	-0.746975
C	-8.682588	1.176869	0.757891
H	-8.906721	2.094454	1.296482
N	5.123576	0.199727	0.122139

O	6.259467	0.267558	0.187443
C	-3.649737	0.677289	0.388534
H	-3.189385	1.518413	0.900333
C	-4.853580	-1.541388	-0.869192
H	-5.307961	-2.393013	-1.367599
C	-5.028348	0.563695	0.342044
C	-3.469361	-1.431996	-0.809421
H	-2.859618	-2.194956	-1.284997
C	-5.637919	-0.542225	-0.287659
C	-6.082376	1.487718	0.900871
H	-6.011675	2.496972	0.473337
H	-5.986907	1.605920	1.988693

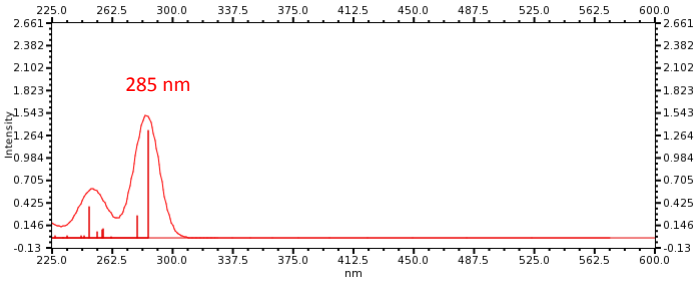
Trans(Cl-Cl)-[Ru(terpyridine)(Cl)2(NO)]+

Ru	3.362530	0.086893	0.029192
Cl	3.309716	-0.085439	-2.375841
Cl	3.101714	0.237813	2.422070
N	1.355576	-0.050127	-0.048584
C	0.643578	1.086018	-0.155997
C	1.469140	2.302276	-0.202150
N	3.081340	-1.980059	0.156259
H	-2.435560	-0.308957	-0.195501
N	2.814069	2.097203	-0.130027
C	3.185091	4.451283	-0.272545
H	3.899010	5.266722	-0.296534
C	0.798211	-1.272934	0.009638
C	-0.588683	-1.393833	-0.042342
H	-1.067744	-2.364197	0.002266
C	3.756308	-4.262727	0.339312
H	4.570295	-4.973852	0.422511
C	1.775161	-2.366130	0.125644
C	-1.354014	-0.235117	-0.153588
C	0.948962	3.587129	-0.311266
H	-0.122352	3.738162	-0.367886
C	-0.746737	1.017310	-0.211641
H	-1.348180	1.913905	-0.298122
C	3.647763	3.144220	-0.164425
H	4.707573	2.931731	-0.104164
C	4.044260	-2.904416	0.260281
H	5.066893	-2.549754	0.280720
C	1.427316	-3.710245	0.201121
H	0.385261	-4.005563	0.175842
C	2.428622	-4.671541	0.309296
H	2.169319	-5.723317	0.368917
C	1.815879	4.675973	-0.347042

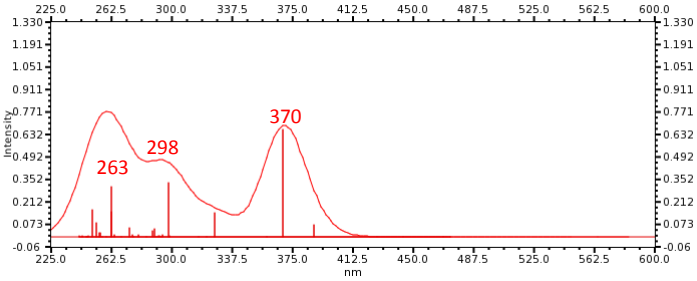
H	1.421609	5.683128	-0.431990
N	5.119625	0.206855	0.097284
O	6.255170	0.284381	0.141290

S4. CAM-B3LYP computed DFT spectra for FT, *trans*(Cl-Cl)-[Ru^{II}(FT)$(Cl)_2$(NO)]$^+$, and *cis*(Cl-Cl)-[Ru^{II}(FT)$(Cl)_2$(NO)]$^+$.

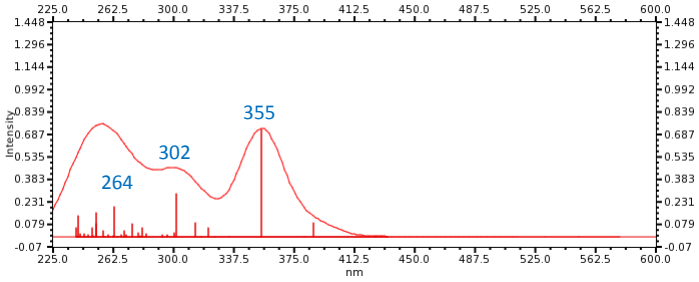
TF



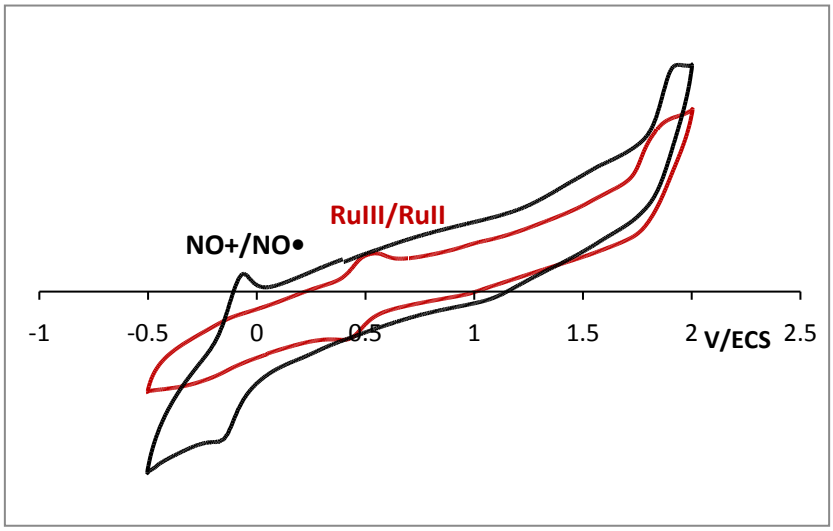
trans(Cl-Cl)-[Ru^{II}(FT)$(Cl)_2$(NO)]$^+$



cis(Cl-Cl)-[Ru^{II}(FT)$(Cl)_2$(NO)]$^+$



S5. Voltamogram of *trans*(Cl,Cl)-[Ru(FT)Cl_2(NO)](PF_6)



Trans(Cl,Cl)-[Ru(FT)Cl_2(NO)](PF_6) (black) and photoproduct (red)