# 2D-IR spectroelectrochemistry of singly oxidized *cis*-[Ru(4,4'-(MeO)$_2$-bpy)$_2$(NCS)$_2$] and reduced *cis*-[Ru(4,4'-(COOEt)$_2$-bpy)$_2$(NCS)$_2$] (bpy = 2,2'-bipyridine) complexes

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Vibrational and solvation relaxation dynamics, and vibrational coupling pathways of the title photosensitizer complexes were investigated on LIFEtime, using an air-tight transmittance spectroelectrochemical cell optimized for suppressed laser-light scattering (Spectroelectro-chemistry Reading).

Measured pump-probe 2D-IR ν(NCS) spectra of cis-[Ru(bis(MeO)-bpy)$_2$(NCS)$_2$] in the ground state exhibit two-component vibrational relaxation for parallel/perpendicular polarizations – ultrafast (0.45/- ps) and long-lived (56/65 ps). The corresponding relaxation times for the Ru-based monocation are dramatically shorter, 0.15/0.35 ps and 3.0/4.0 ps, respectively. Negligible acceleration of the ν(NCS) vibrational relaxation was determined for reduced cis-[Ru(4,4'-(COOEt)$_2$-bpy)$_2$(NCS)$_2$] where the extra electron is localized at the ester-bpy ligand. The time constant for spectral diffusion decreased markedly (ca six-times) only for the largely Ru-based oxidation of the bis(OMe)-bpy complex.

Electronic-structure (G16/PBE0) and anharmonic-frequency (VPT2) quantum-chemical calculations conducted on the ground states, doublet redox states and related triplet MLCT excited states of the title complexes provided a good match with the experiment, including diagonal and off-diagonal anharmonicities.

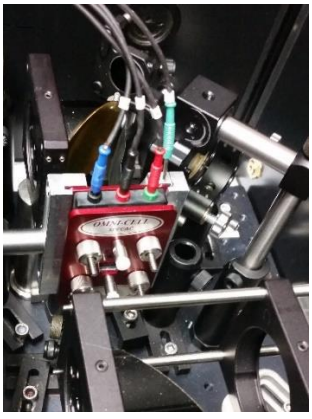

*Figure 1: LIFEtime-OTTLE cell setup used for the 2D-IR spectroelectrochemical experiments.*

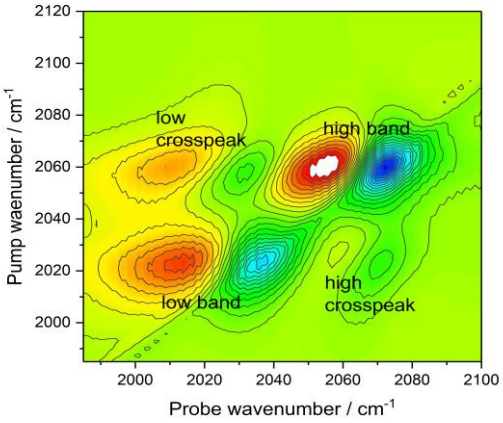


*Figure 2: Representative 2D-IR spectrum of in situ generated cis-[Ru(4,4'-(MeO)$_2$-bpy)$_2$(NCS)$_2$]$^+$ in DMF.*