Simulation of the resonance Raman intensities of a Ruthenium-Palladium photocatalyst by time dependent density functional theory

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Supplementary Information

- The absorption spectrum, excited states and molecular orbitals calculated with the CAM-B3LYP functional in vacuum are presented on Fig. S1, Table S1 and Table S2, respectively.
- A comparison between the RR spectrum and the normal Raman spectrum is provided on Fig. S2.

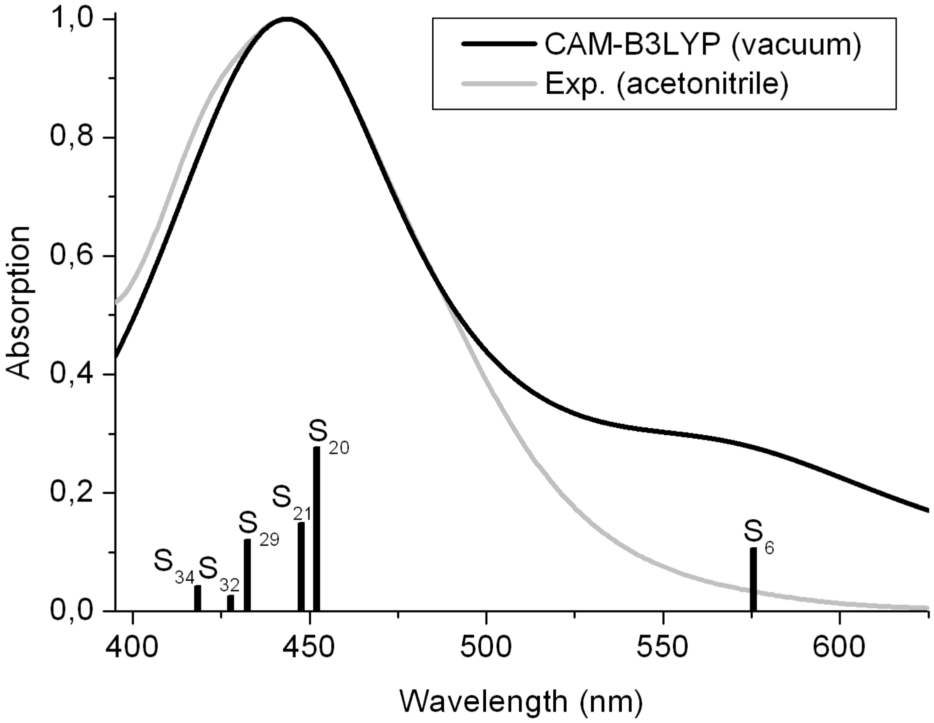
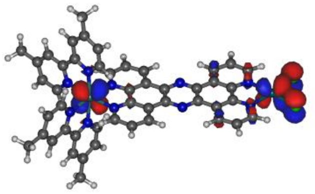
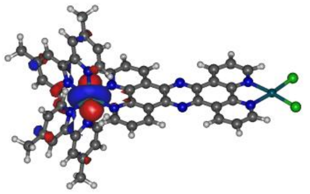
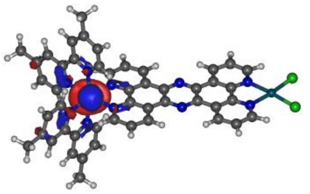
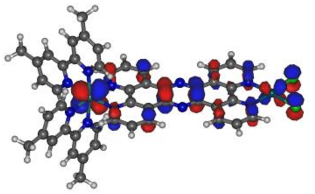
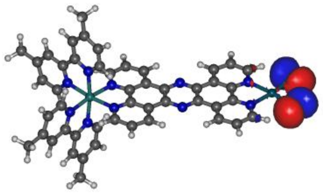
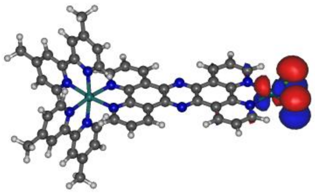
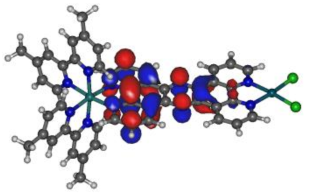
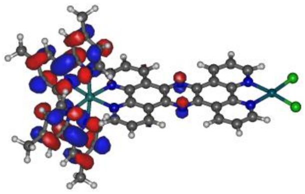
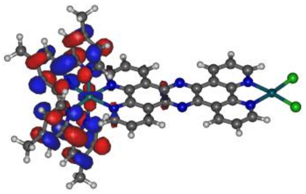
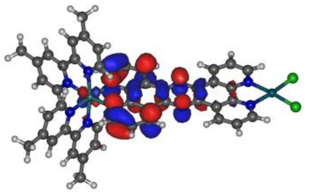
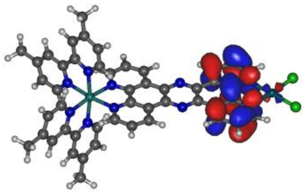
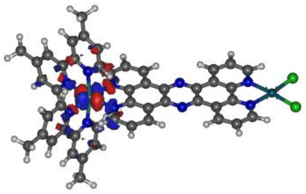
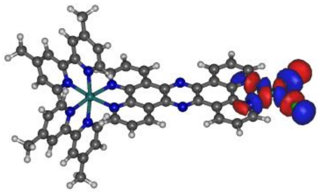
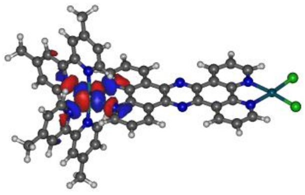


Figure S1: Absorption spectrum and oscillator strengths of $[(tbbpy)_2Ru(tpphz)PdCl_2]^{2+}$ calculated with CAM-B3LYP in vacuum. The theoretical spectrum is computed with a damping factor Γ fixed at 2000 cm^{-1} and is shifted so that experimental and theoretical maxima coincide.

Table S1: Vertical excitation energies (E^e), oscillator strengths (f) and singly-excited configurations with weights larger than 5% of the main excited states contributing to the first absorption band. The calculations are performed with the CAM-B3LYP functional in vacuum.

State number	Transition	Weight (%)	E^e (eV)	f
6	H-2 → L H-2 → L+3 H-2 → L+1 H-2 → L+6	64 17 8 5	2.89	0.107
20	H-5 → L H-9 → L H-7 → L+2 H-5 → L+3 H-8 → L+2 H-9 → L+3	38 12 8 8 6 6	3.48	0.277
21	H-2 → L+6 H-2 → L	64 13	3.50	0.149
29	H-8 → L+1 H-8 → L H-7 → L+20	69 7 6	3.60	0.121
32	H-3 → L+17	93	3.63	0.026
34	H-7 → L+20 H-7 → L+15 H-8 → L+20 H-5 → L+2 H-8 → L+1 H-9 → L+2	26 12 10 8 7 6	3.70	0.043

Table S2: Molecular orbitals involved in the dominant configurations of the states responsible for the absorption spectrum of the complex (CAM-B3LYP, vacuum).

 H-9	 H-8	 H-7
 H-5	 H-3	 H-2
 L	 L+1	 L+2
 L+3	 L+6	 L+15
 L+17	 L+20	

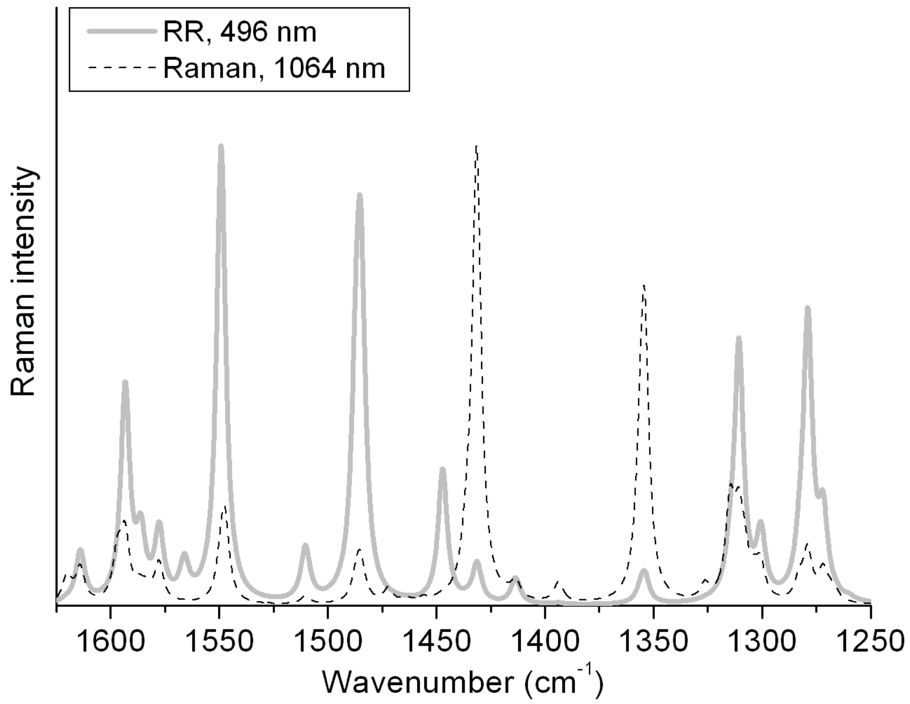


Figure S2: Comparison between the normal Raman spectrum for an excitation wavelength of 1064 nm and the RR spectrum for an excitation wavelength of 496 nm. The calculations are performed with the B3LYP functional in acetonitrile (IEFPCM).

The normal Raman differential cross-sections were calculated from the Raman polarizability tensor evaluated in the double harmonic approximation

$$(\alpha_{\alpha\beta})_{g0\rightarrow g1_l} = \sqrt{\frac{\hbar}{2\omega_l}}\left(\frac{\partial\alpha_{\alpha\beta}}{\partial Q_l}\right)_0 .$$

The analytical polarizability derivatives at 1064 nm were obtained from the vibrational frequency calculation performed with GAUSSIAN 09.