

Supporting Information

Spectroscopic and Second-order Nonlinear Optical Properties of Ruthenium(II) Complexes: A DFT/MRCI and ADC(2) Study

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Table S1. Excited-state composition of the FDAES of complex 4 at the ADC(2) and ADC(2)/COSMO levels.

ADC(2)

| State | ΔE (eV) | f | Assignment (coeff.) |
|----------------|-----------------|------|-----------------------|
| S ₁ | 2.99 | 1.68 | H→L $\pi\pi^*$ (0.83) |

ADC(2)/COSMO

| State | ΔE (eV) | f | Assignment (coeff.) |
|----------------|-----------------|------|-----------------------|
| S ₁ | 2.12 | 0.29 | H-1→L MLCT (0.69) |
| | | | H→L $\pi\pi^*$ (0.41) |
| | | | H-1→L+1 MLCT (-0.41) |

Table S2. Basis set dependence of selected electronic transition energies (in eV) and oscillator strengths (in parentheses) of complex 1 and 2 at the DFT/MRCI and ADC(2) levels of theory.

| Complex | State | DFT/MRCI/ def2-SVP | DFT/MRCI/ def2-TZVP | ADC(2)/ def2-SVP | ADC(2)/ def2-TZVP |
|---------|-------|-----------------------|------------------------|---------------------|----------------------|
| 1 | FDAES | 2.80 (0.297) | 2.86 (0.296) | 3.03 (0.12) | 2.72 (0.10) |
| 2 | FDAES | 2.80 (0.537) | 2.82 (0.545) | 3.11 (0.23) | 2.80 (0.19) |

Figure S1. Main BH-LYP orbitals involved in the FDAES of complex 3 and 4.

