Charge Separation Mechanisms and Lifetimes from TDDFT and Nonadiabatic Dynamics

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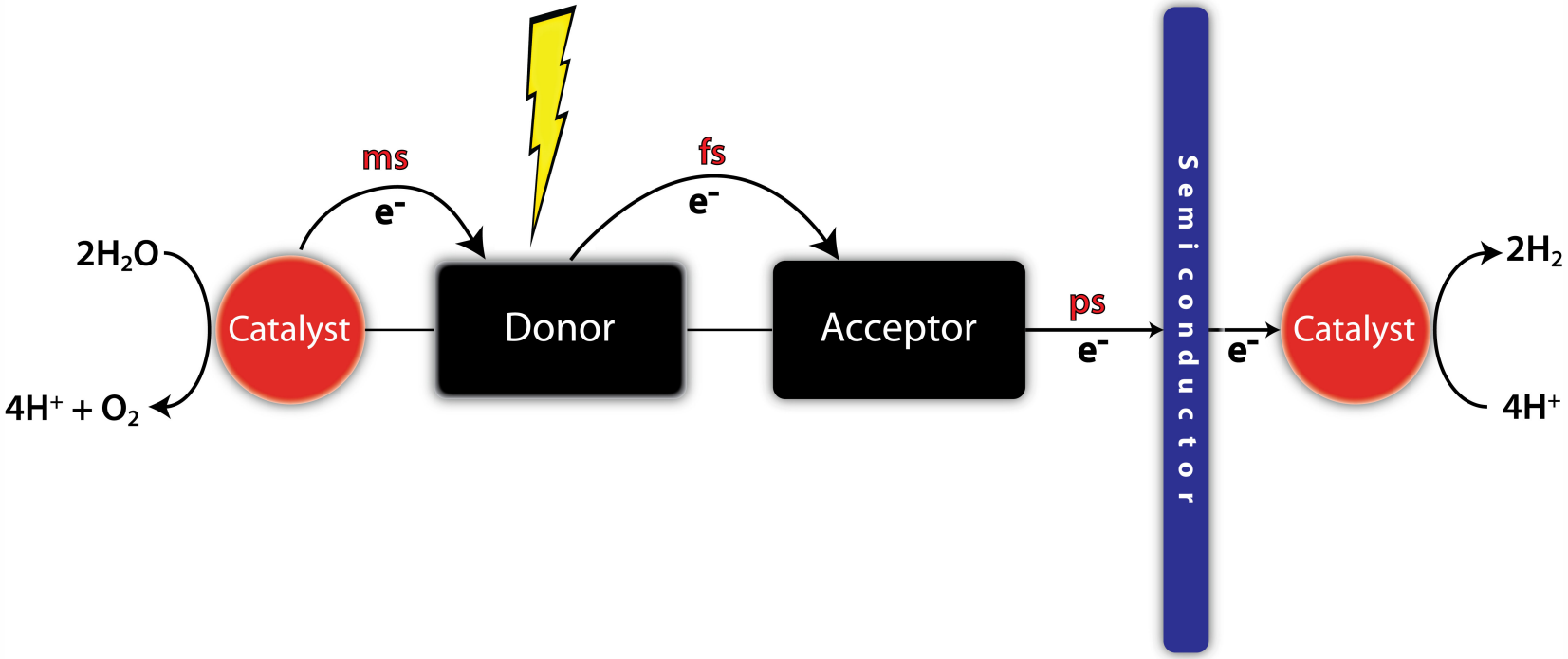
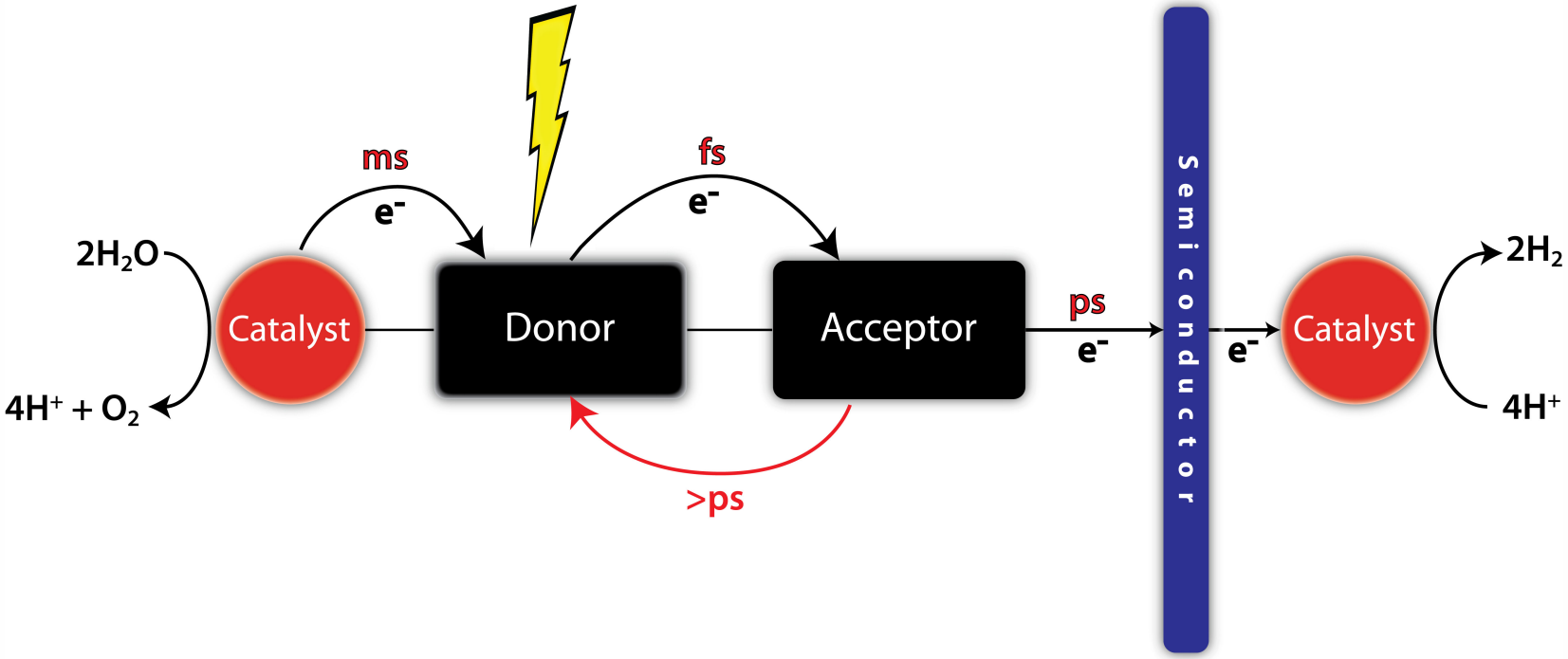
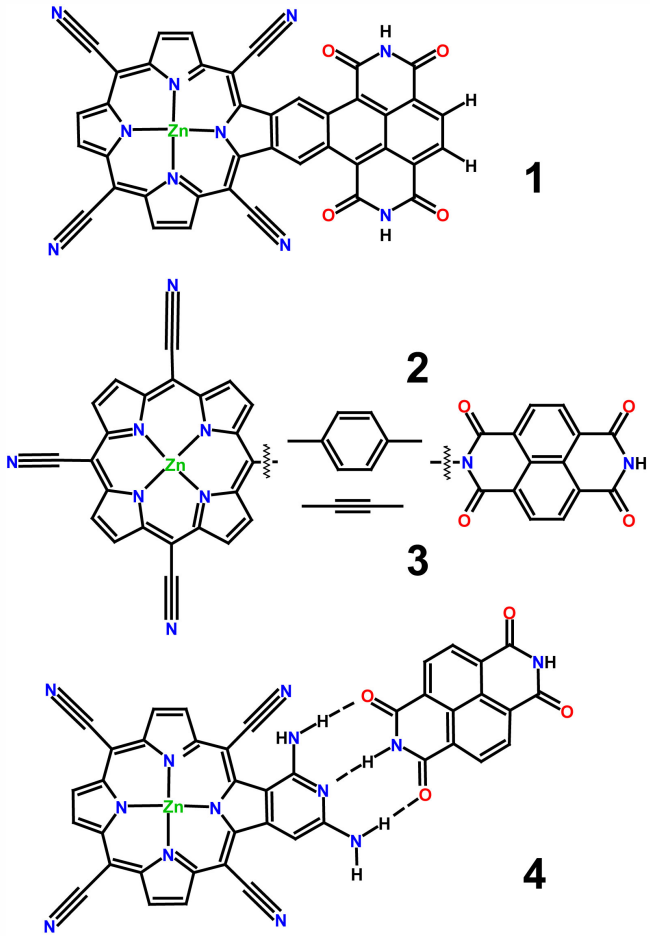
Introduction

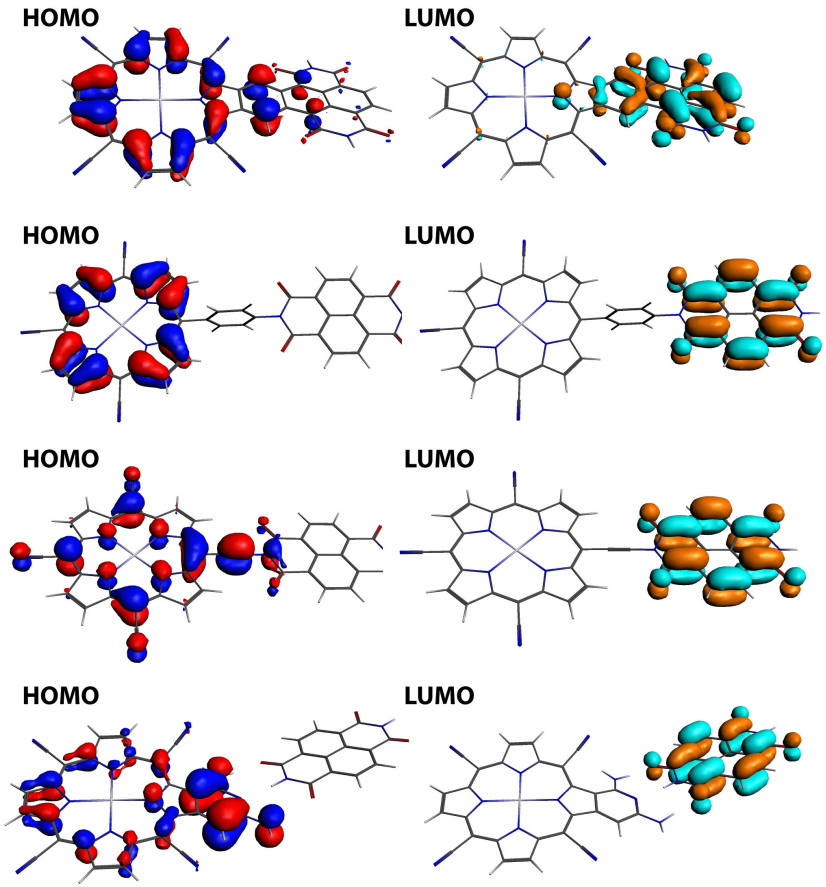


Introduction



Molecular Dyads





Oxidation Potentials

GSOP

$$GSOP = (G^0 - G^+)_{GS,aq}$$

>0.86 H_2O Catalyst

Oxidation Potentials (aq, vs NHE)

Ground State Oxidation Potentials (eV)

1: 1.45 **2**: 1.33 **3**: 1.33 **4**: 1.45

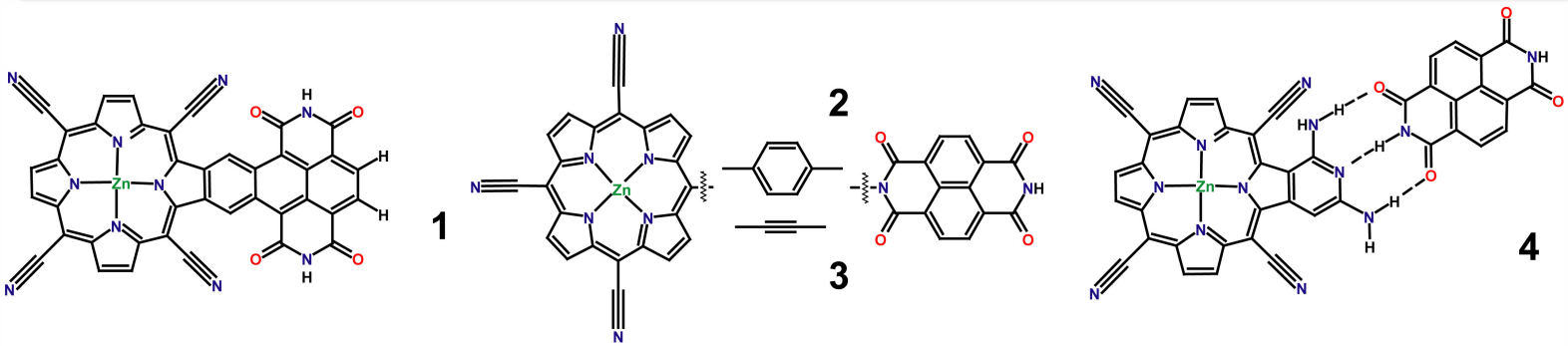
Excited State Oxidation Potentials (eV)

1: -0.67 **2**: -0.67 **3**: -0.67 **4**: -0.67

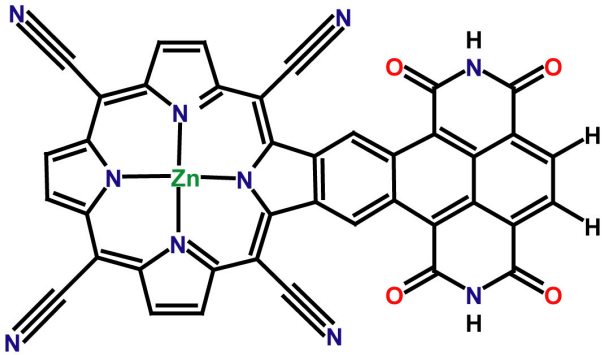
H_2 Catalyst <-0.37

ESOP

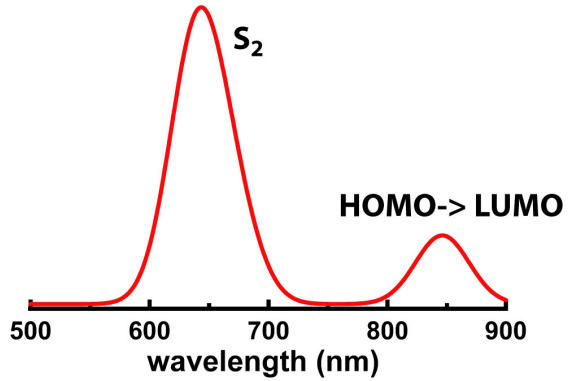
$$ESOP = (G^0 - G^+)_{ES,aq} \approx (G^0 - G^+)_{GS,aq} - E_{0-0,aq}$$



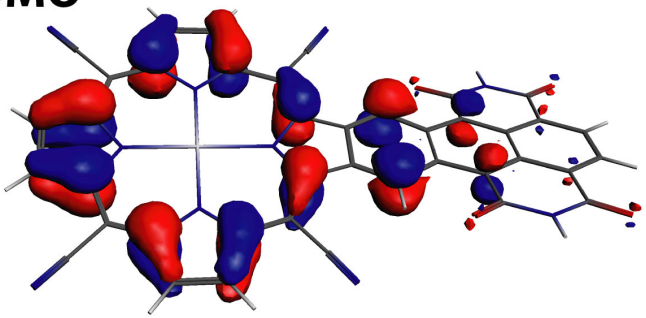
TDDFT; Complex 1



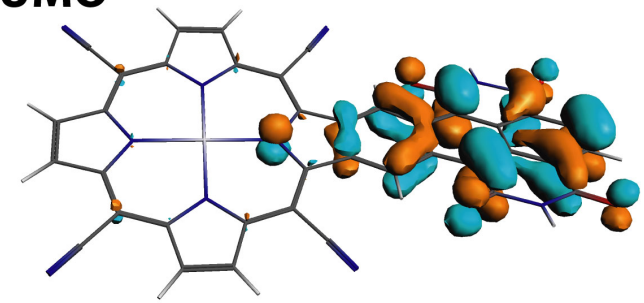
1



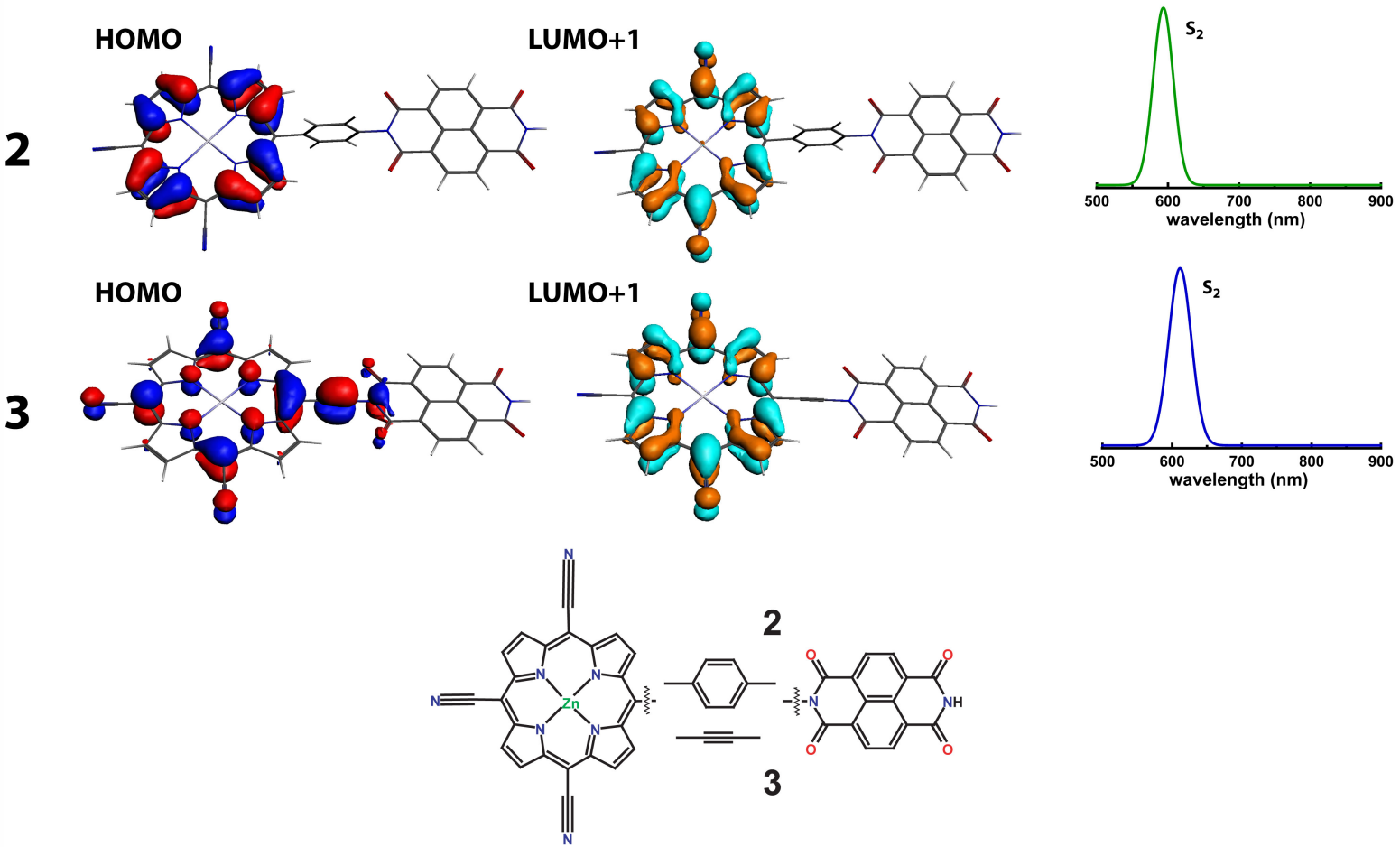
HOMO



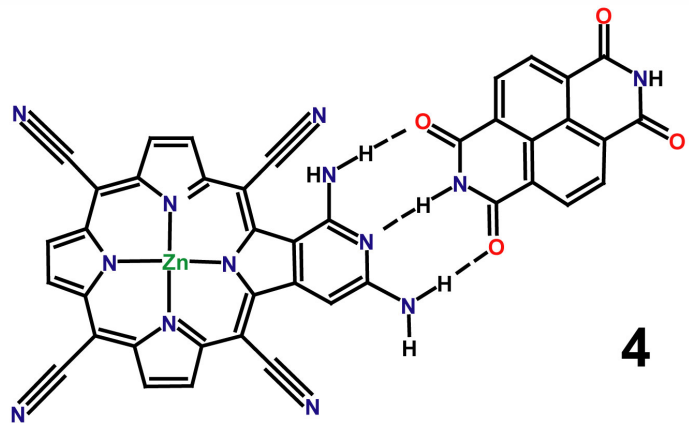
LUMO

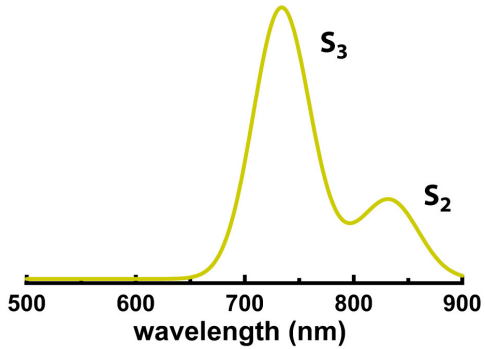


TDDFT; Complex 2 and 3

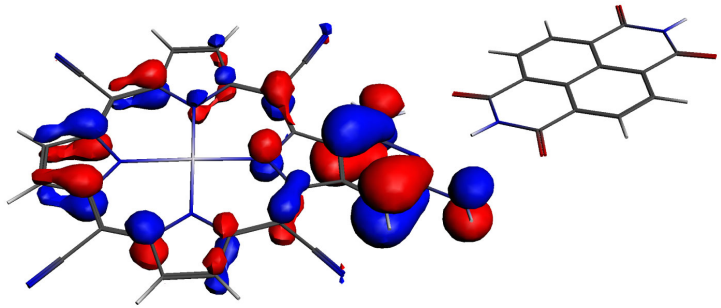


TDDFT; Complex 4

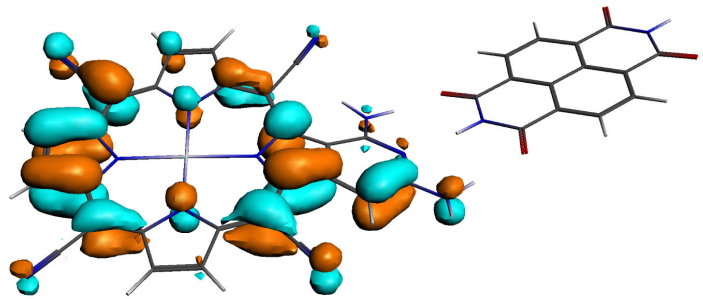




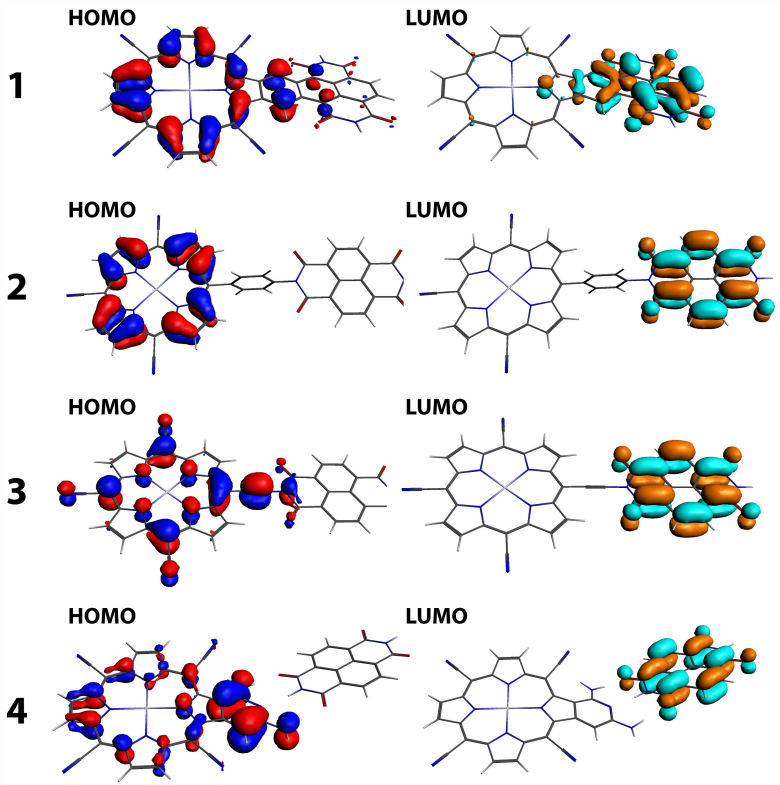
HOMO



LUMO+2



AIMD of Charge Recombination



AIMD

$$M_i \frac{d^2 R_i}{dt^2} = -\nabla_i \langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle$$

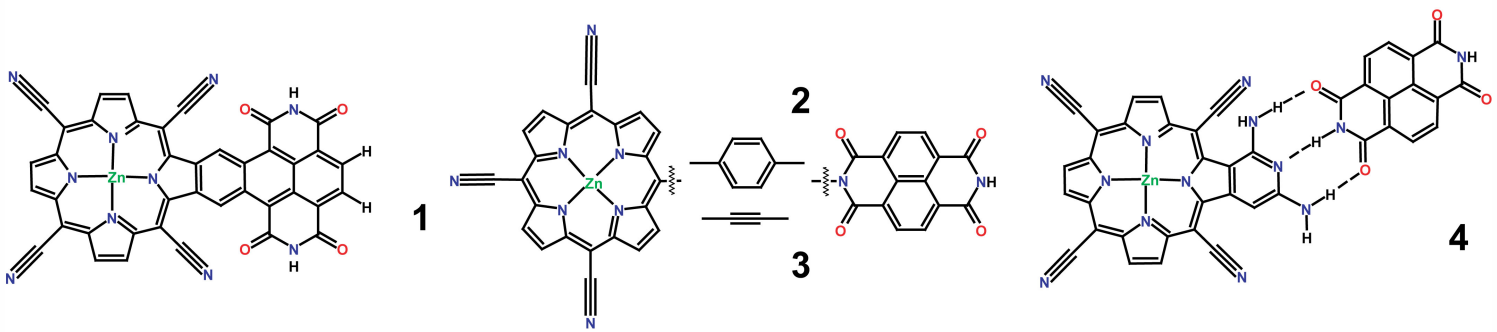
$$\mathcal{H}_e \Psi_0 = E_0 \Psi_0$$

ROKS

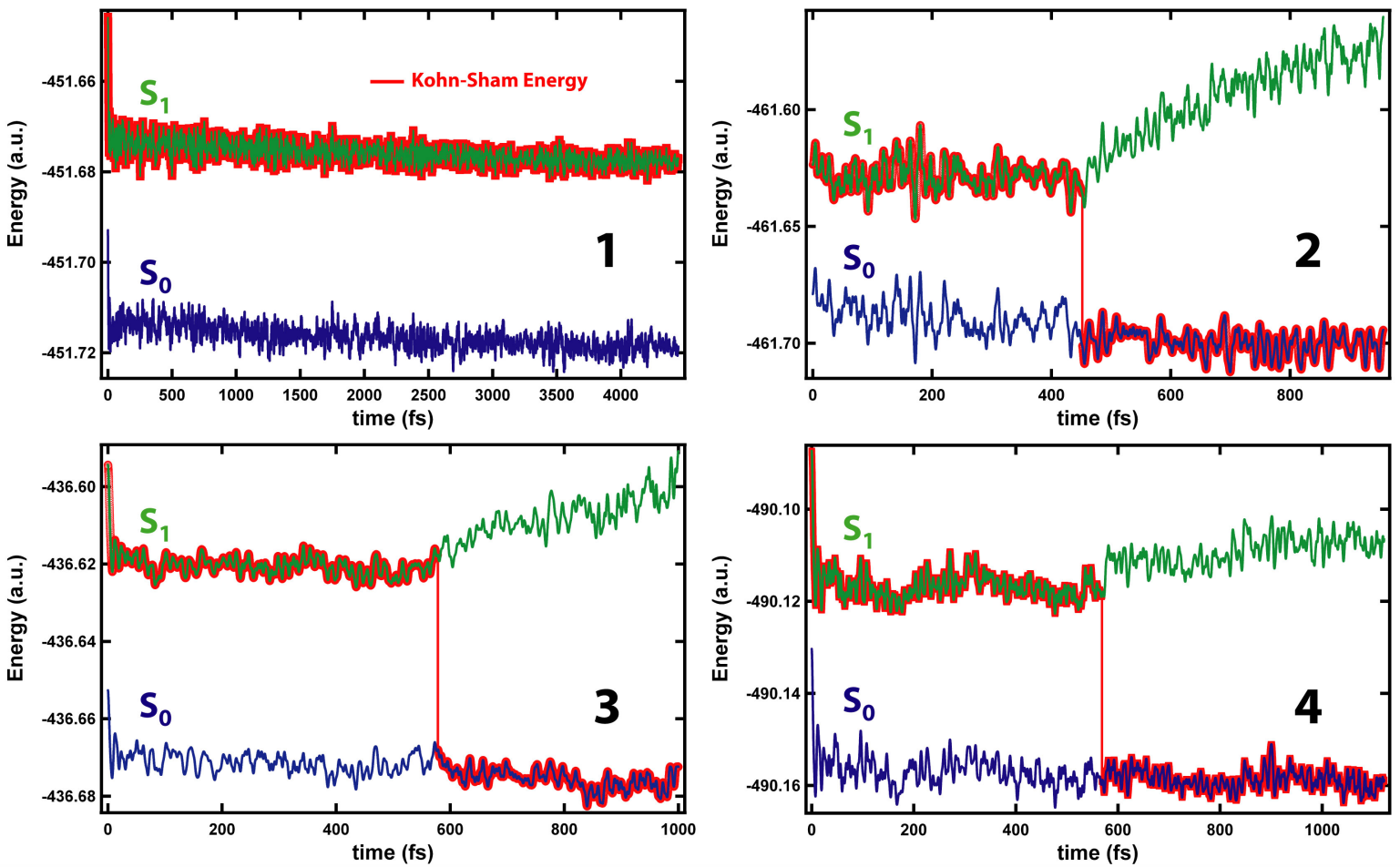
$$E(S_1) = 2E(m) - E(t)$$

TDDFT vs ROKS; long range CT

(eV)	ROKS	TDDFT	HOMO-LUMO
1	1.277	1.265	1.106
2	1.508	1.073	1.073
3	1.585	0.728	0.729
4	1.170	0.560	0.531



Nonadiabatic Dynamics with ROKS



Conclusions

- A computational framework for characterizing artificial photosynthetic modules in terms of oxidation potentials, optical absorption and charge separation/recombination is presented and validated on a series of molecular dyads.
- Complex **1** appears to meet the requirements as charge separation module the best.

Acknowledgements

- Dr. Francesco Buda
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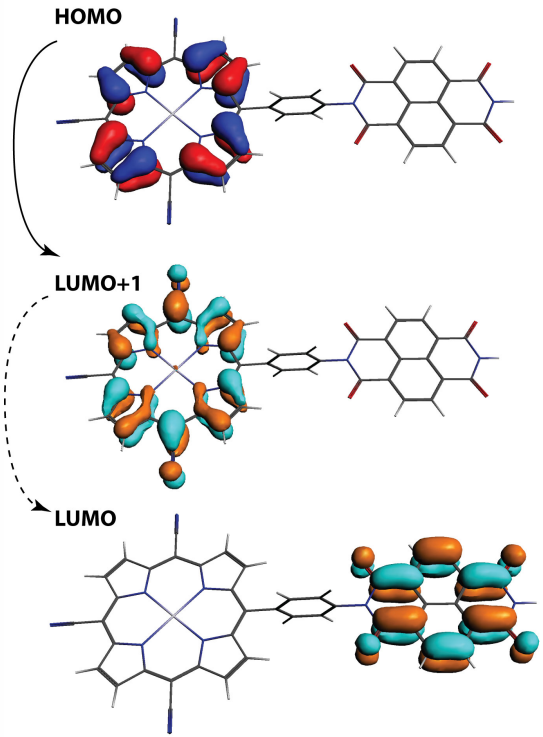
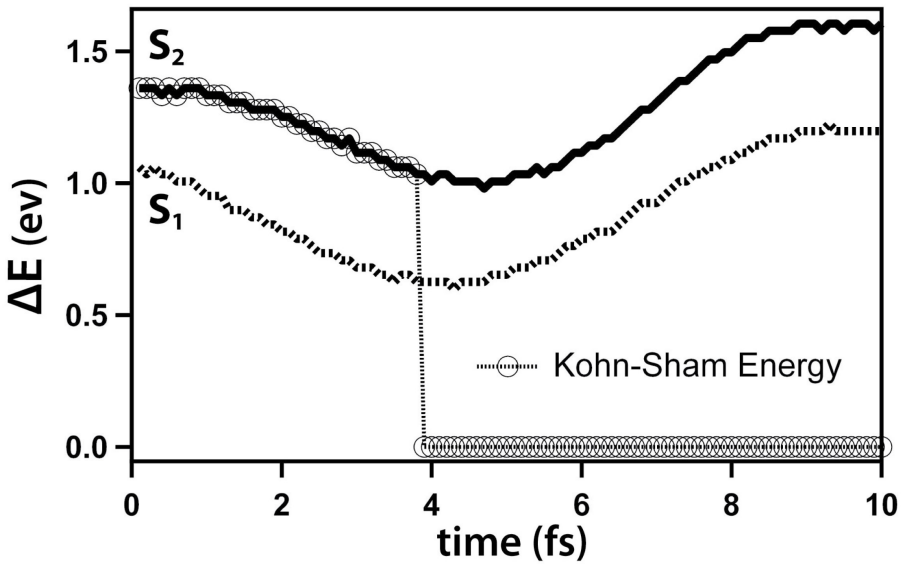
Nonadiabatic Dynamics with TDDFT of Charge Separation?





Nonadiabatic Dynamics with TDDFT of Charge Separation?