

Abstract: The light-induced magnetic bistability of square pyramidal and octahedral Ni(II) macrocyclic ligand complexes have been investigated using DFT and linear response TD-DFT methods considering the MN12-SX exchange-correlation functional and the def2-TZVP basis set. The theoretical UV spectra of azopyridine functionalized Ni-porphyrin macrocyclic ligand complex for different spin configurations have been compared with the experimental results [1]. The stability of the light-mediated reversible ligand coordination and the switching of magnetic properties have been characterized by identifying the active electronic excited states both in singlet and triplet spin configuration involved in the light-induced excited spin-state trapping. The location of the intersystem crossing points between different spin states has been also performed. Finally, a detailed theoretical description of the spin crossover phenomena in the square pyramidal and octahedral Ni(II) macrocyclic ligand complex is presented.

Method:

- The equilibrium geometries of the azopyridine functionalized Ni-tetrakis(pentafluorophenyl)-porphyrin (AP-Ni-TPP) and biazopyridine functionalized Ni-tetrabenzene-porphyrin (biAP-Ni-TBP) have been obtained using the MN12-SX [2,3] exchange-correlation functional methods.
- The UV-Vis absorption spectra were computed using the time-dependent density functional (TD-DFT) method with Tamm-Dancoff approximation.
- The ISC points were localized through the "Penalty Function" Algorithm [4].

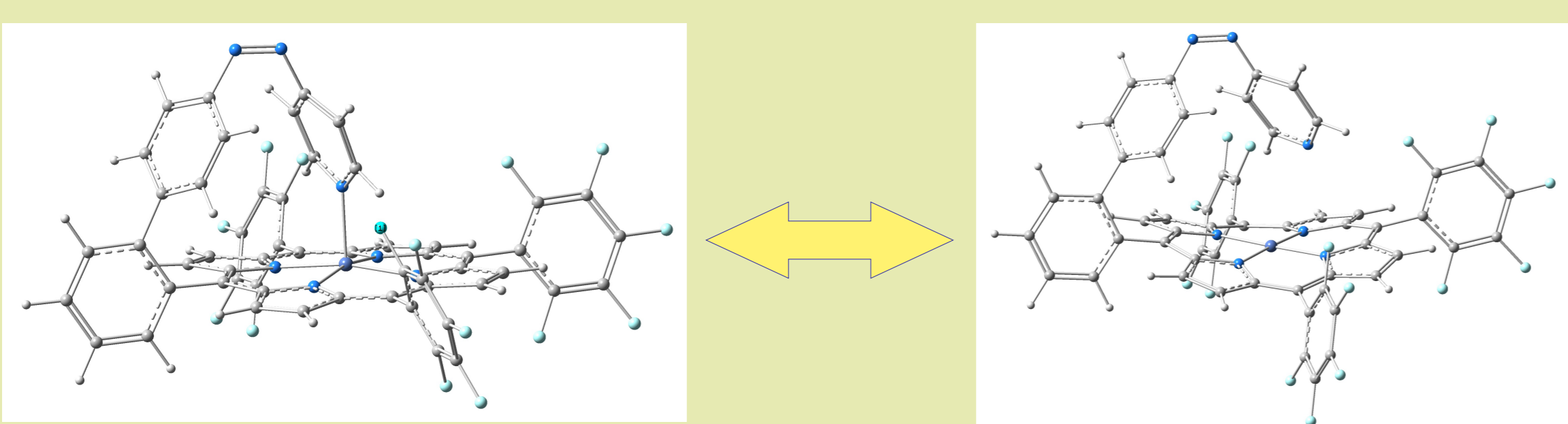


Figure 1. The equilibrium geometry configuration for the triplet - singlet spin transition in square pyramidal Ni(II) macrocyclic ligand complex.

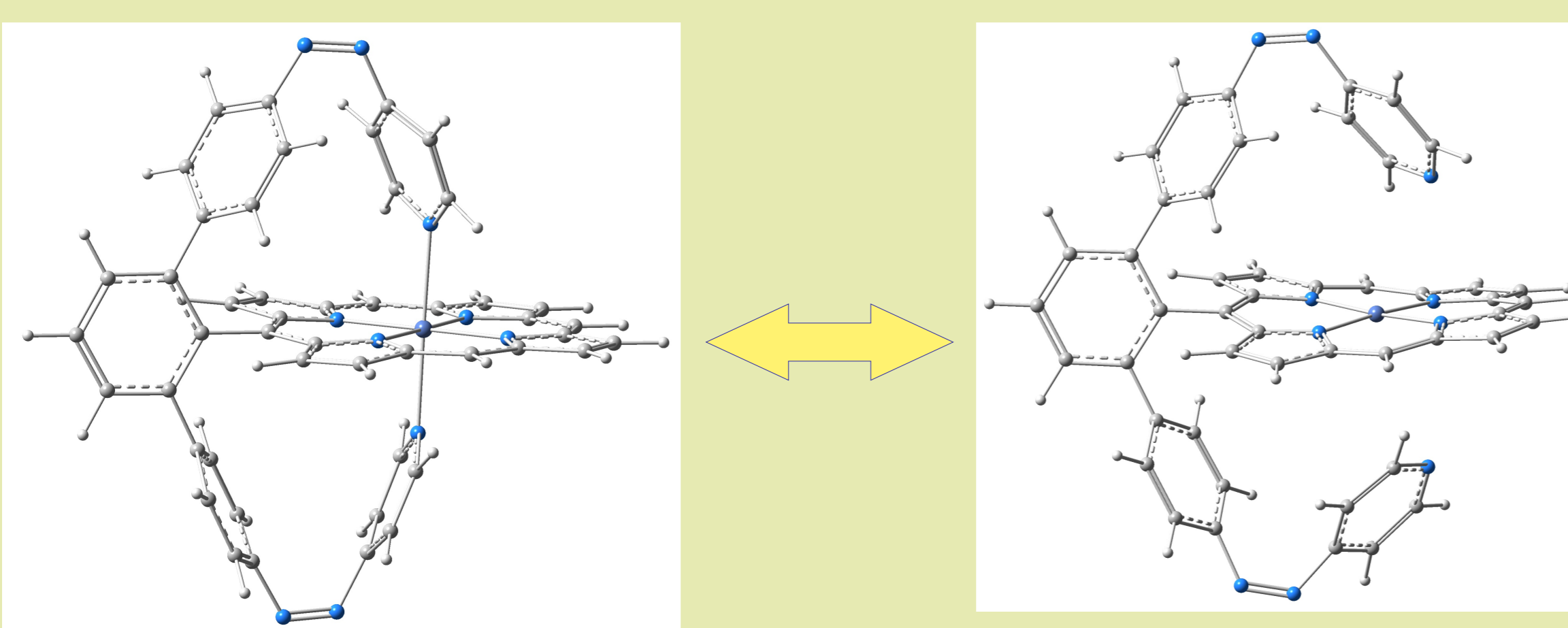


Figure 2. The equilibrium geometry configuration for the triplet - singlet spin transition in octahedral Ni(II) macrocyclic ligand complex.

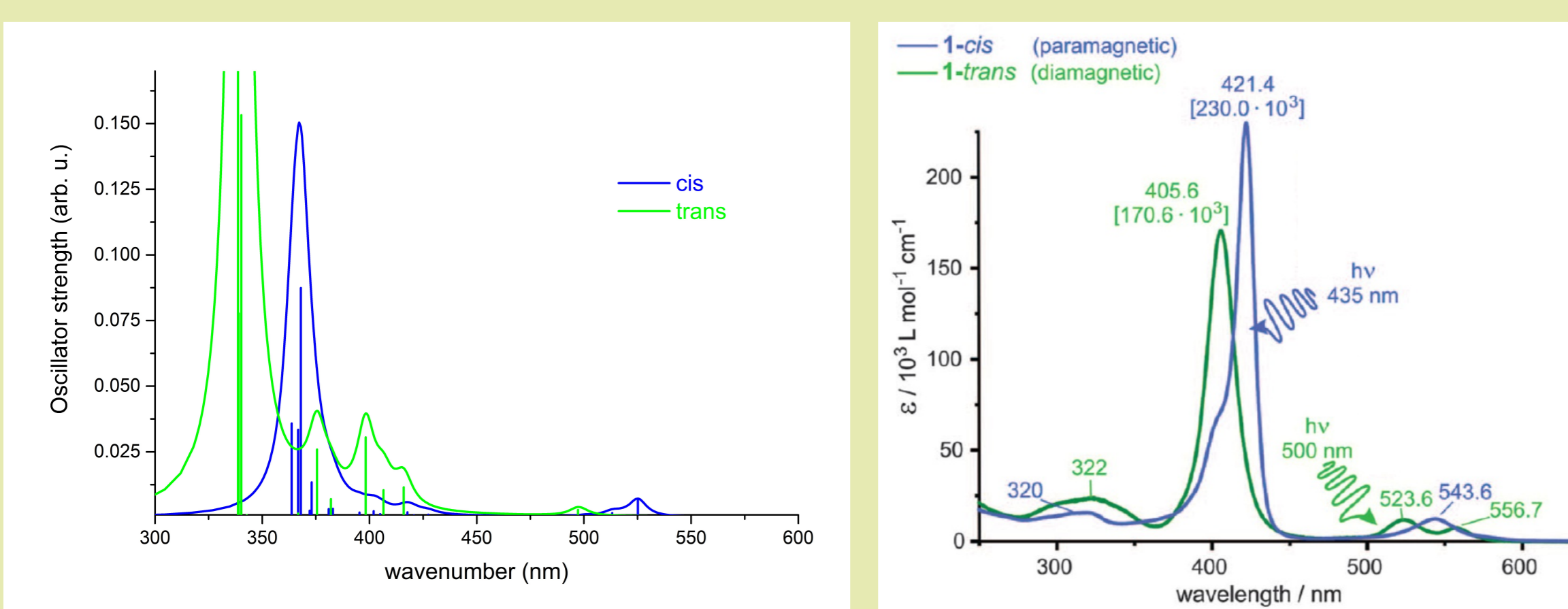


Figure 3. The theoretical (a) and experimental (b) UV-Vis absorption spectra for azopyridine functionalized Ni-tetrakis(pentafluorophenyl)-porphyrin (AP-Ni-TPP) obtained with MN12-SX/def2-TZVP exchange-correlation functional/basis set methods.

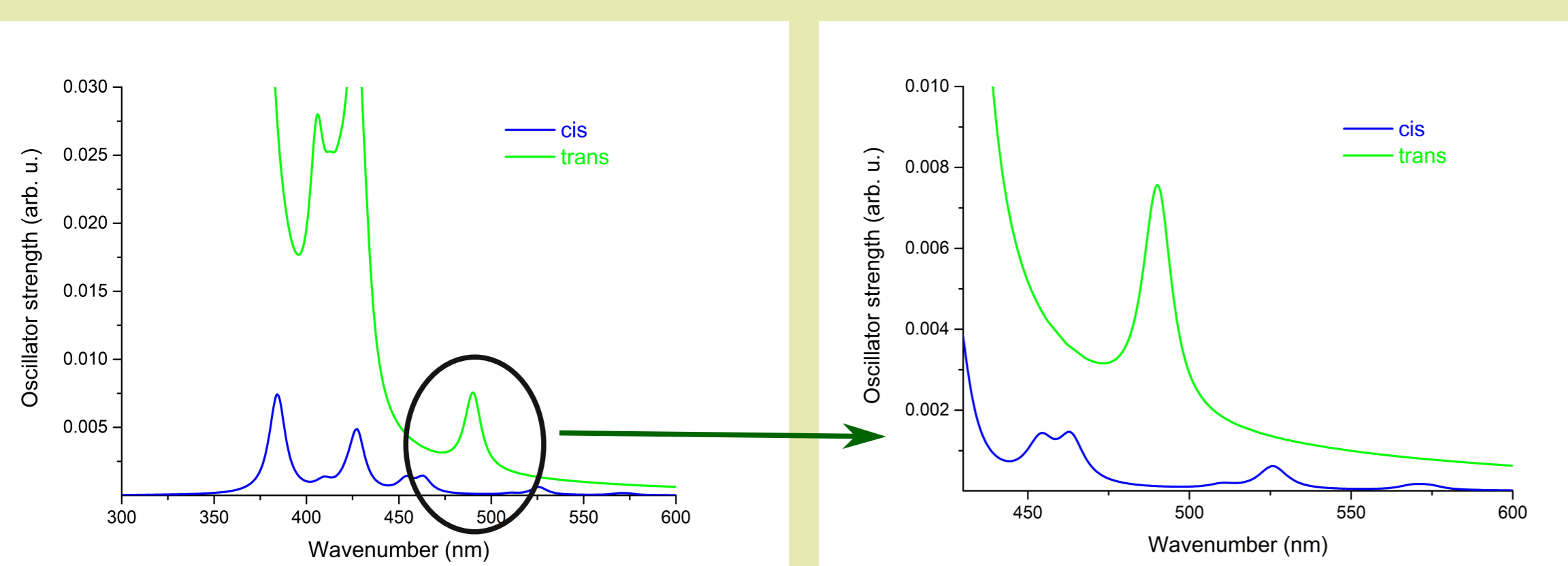


Figure 4. The theoretical UV-Vis absorption spectra for biazopyridine functionalized Ni-tetrabenzene-porphyrin (biAP-Ni-TBP) obtained with MN12-SX/def2-TZVP exchange-correlation functional/basis set methods.

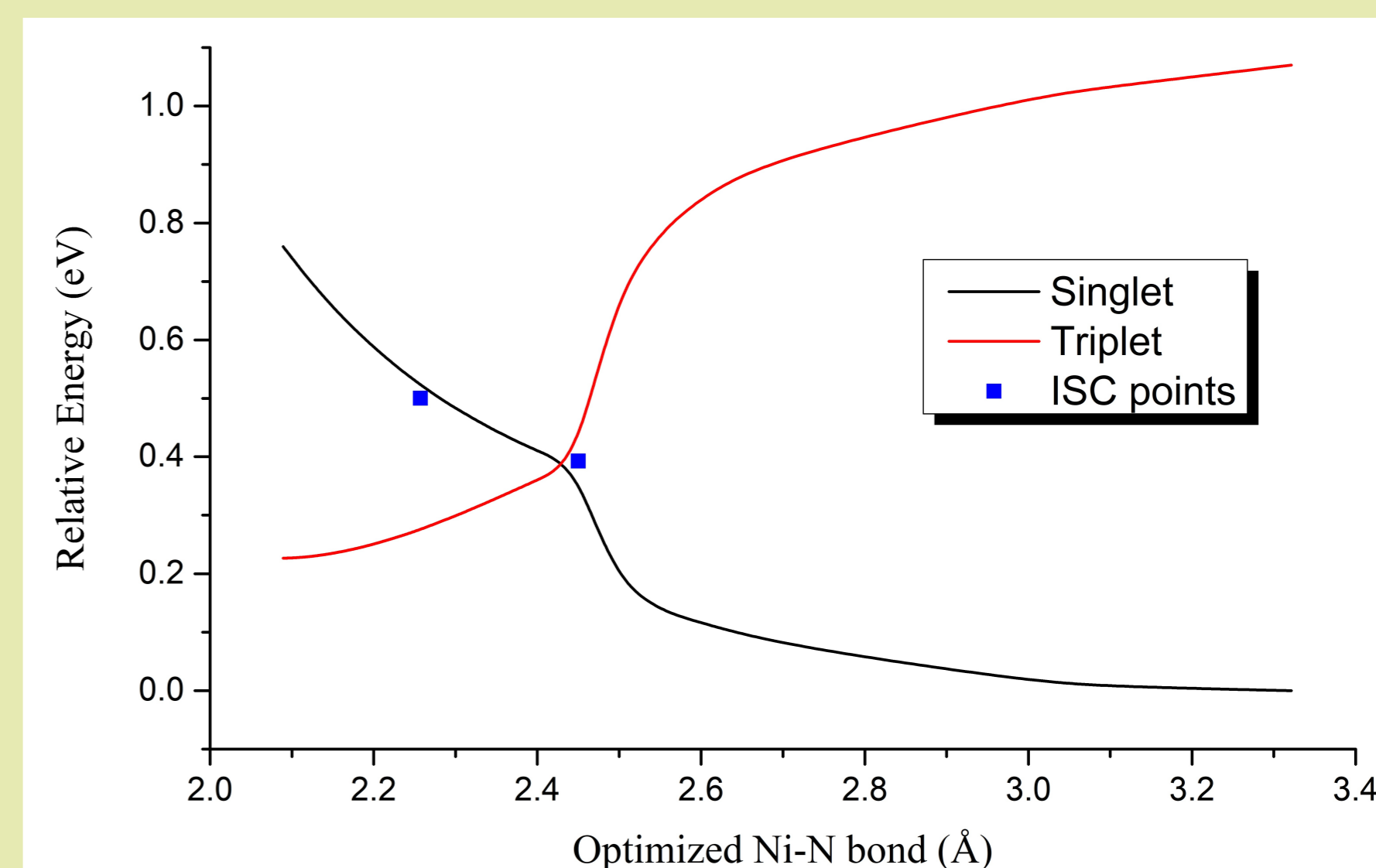


Figure 5. The triplet and singlet potential energy curves along the optimized Ni-N bond and the intersystem crossing point of the spin transition in square pyramidal AP-Ni(II)-TPP macrocyclic ligand complex.

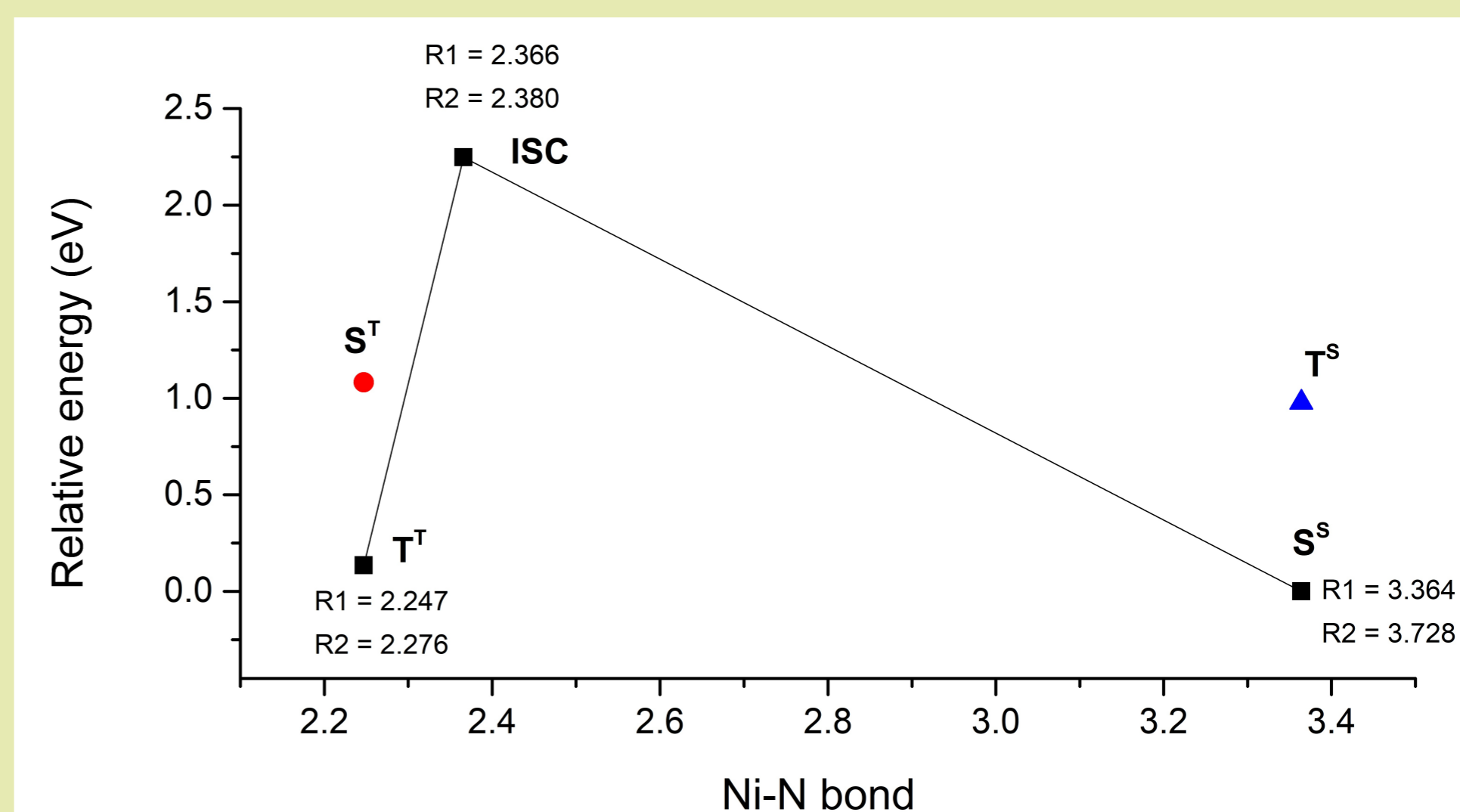


Figure 6. The triplet and singlet energies along the Ni-N bond and the intersystem crossing point of the spin transition in octahedral biAP-Ni(II)-TPP macrocyclic ligand complex.

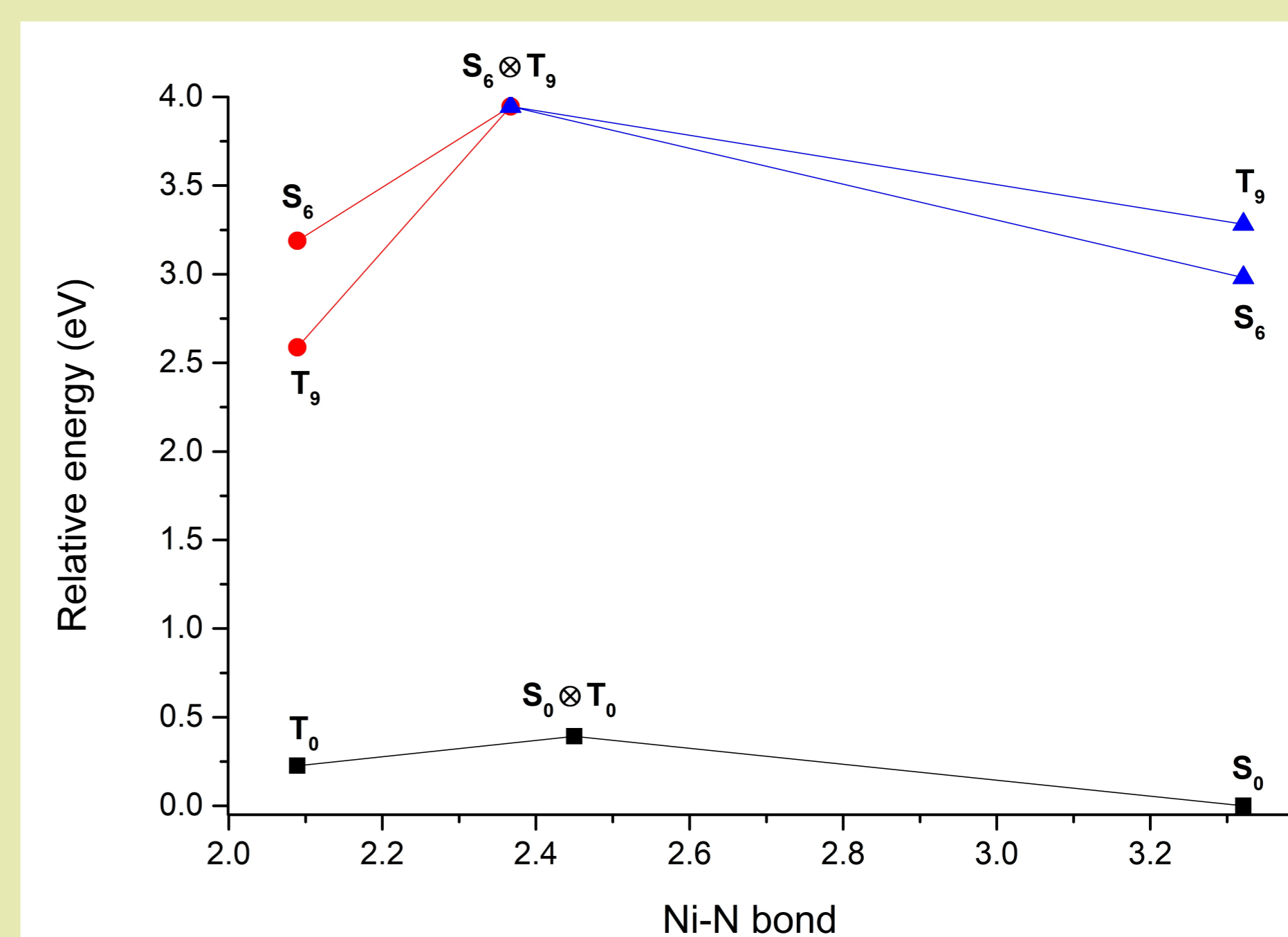


Figure 7. The triplet and singlet ground and excited state energies along the Ni-N bond and the intersystem crossing points of the spin transition in octahedral biAP-Ni(II)-TPP macrocyclic ligand complex.

Acknowledgement

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