Intersystem crossing in metal-ligand coordination complexes with pyramidal-planar and octahedral coordination configurations

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Abstract Materials with "spin crossover" or "spin transition" properties are of major interest through their potential applications such as molecular memory, sensors or molecular switches[1,2]. We have obtained results about the equilibrium geometry optimization and about the searching of intersystem crossing (ISC) points on the potential energy surfaces of the electronic states with singlet and triplet spin states in the case of Ni-Tetrakis(pentafluorophenyl)-porphyrin functionalized with azopiridine (Ni-TPP-AP) as well as in the case of Ni-porphyrin functionalized with two azopiridines (Ni-P-biAP) molecular complexes. The first 30 electronic excited states have been computed at MN12-SX/def2-TZVP level of theory[3,4,5]. We have tailored eight different supramolecular complexes for the studying the spin crossover efficiency. Using the algorithm called "Penalty Function" we have identified the possible intersection points on the hyper-surface of the potential energies for the two singlet and triplet spin configurations. In order to make efficient the searching procedure we have developed a home-made Python code (PyISC) which is able to perform both intersystem crossing and conical intersection point searches either for the ground or the excited state electronic configuration.
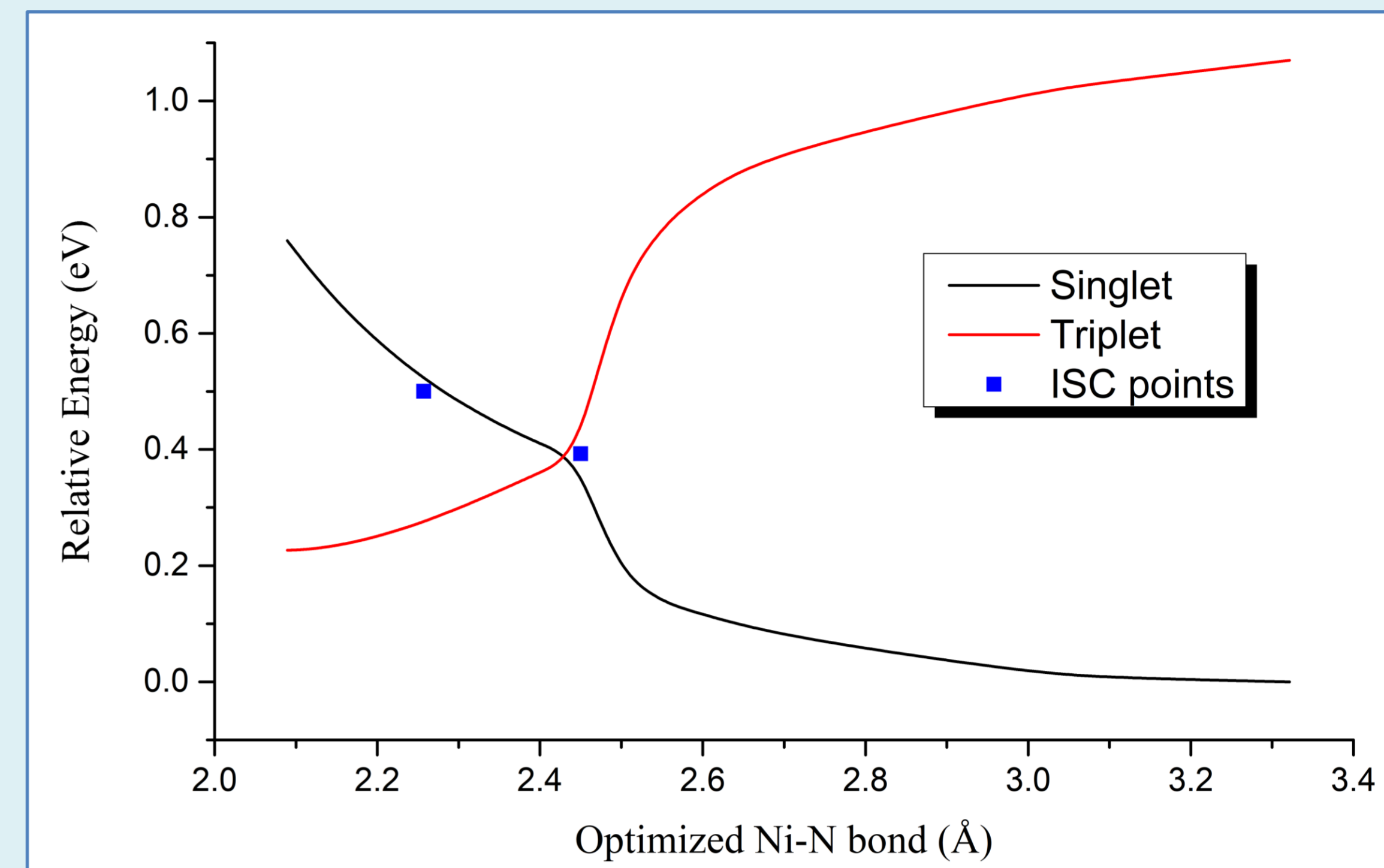
Figure 1. The variation of the relative energy for the triplet and singlet spin states and the position of the ISC points based on different d(Ni···N) distance.

Methods:

The equilibrium geometries of the biazopyridine functionalized Ni-tetrabenzene-porphyrin (biAP-Ni-TBP) have been obtained using the MN12-SX exchange-correlation functional methods. The ISC points were localized through the "Penalty Function" Algorithm. The first term minimises the average of the lower and upper state energies and the second term is the penalty function, which minimises the energy difference. The constant c_1 determines how much weight should be given to these two goals, while c_2 controls how quickly the conical intersection seam is approached.

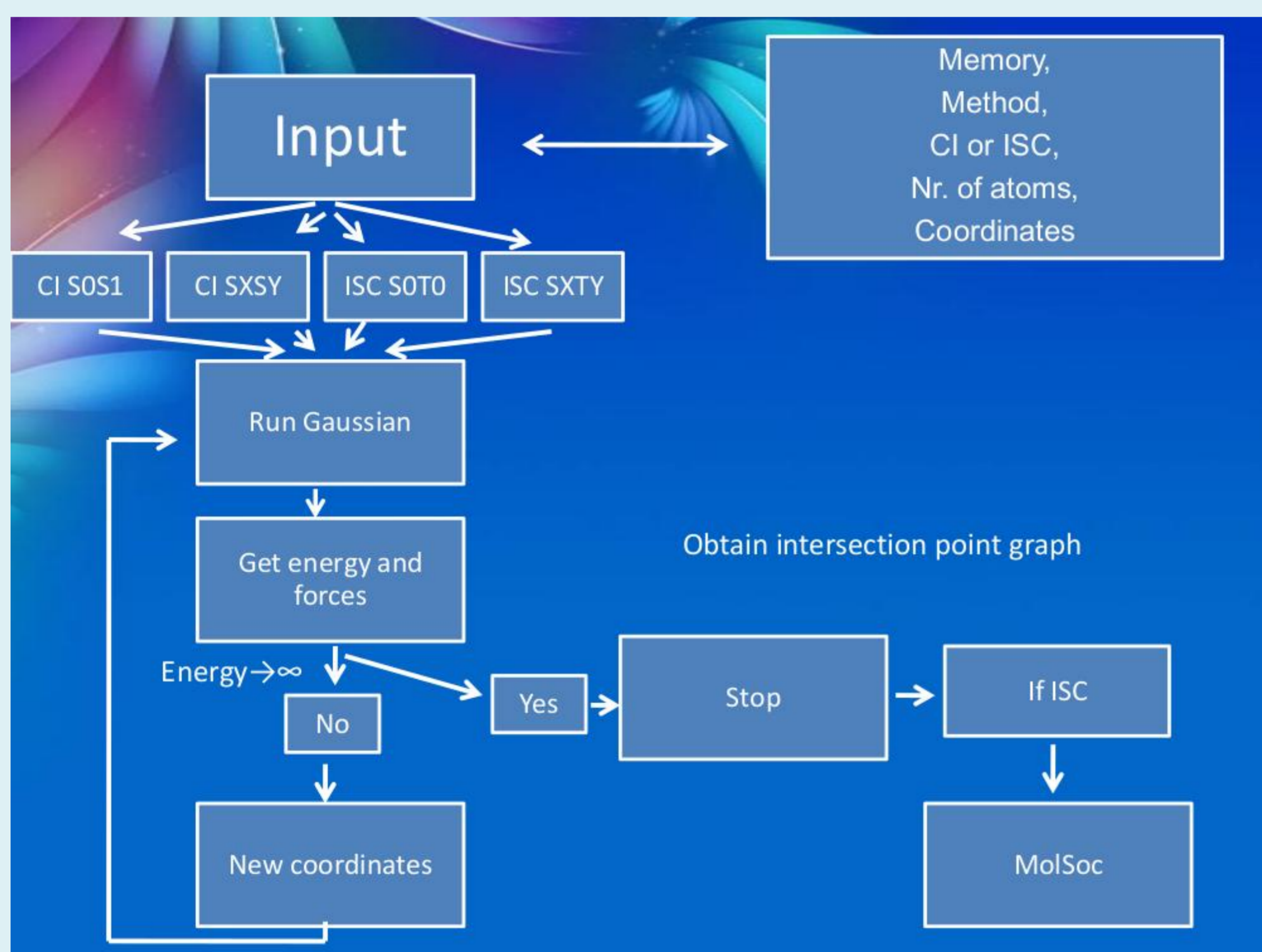$$f(\mathbf{R}) = \frac{E_I + E_J}{2} + c_1 c_2^2 \ln\left[1 + \left(\frac{E_J - E_I}{c_2}\right)^2\right]$$

Figure 2. The logical scheme of the *PyISC* program code.
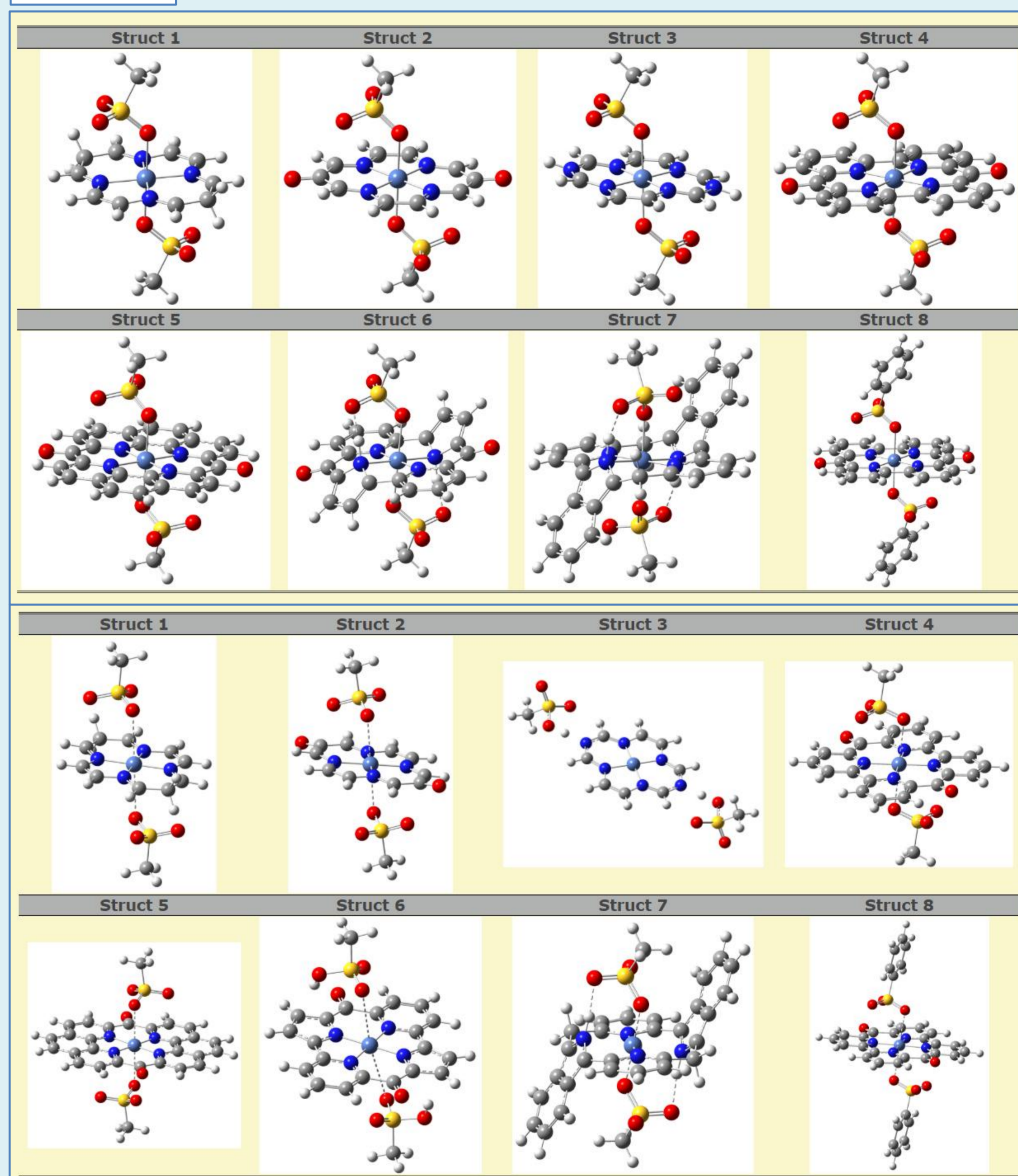
Result:

Table 1. a) The triplet state equilibrium geometries of eight different proposed molecular structures for studying the efficiency of the spin crossover phenomenon. b) The singlet state equilibrium geometries of eight different proposed molecular structures for studying the efficiency of the spin crossover phenomenon.

	Struct 1	Struct 2	Struct 4	Struct 5	Struct 7	Struct 8
$E^{Singlet}$ (H)	-3442.34047057	-3590.33428394	-4050.14601171	-4202.61336492	-4133.11431782	-4433.58368205
R^S(Ni···O) (Å)	2.811	2.640	2.612	2.609	1.924	2.593
$E^{Triplet}$ (H)	-3442.34801587	-3590.35171473	-4050.16632794	-4202.62864037	-4133.14474166	-4433.60380049
R^T(Ni···O) (Å)	2.136	2.109	2.125	2.133	2.109	2.125
E^{S-T} Gap (eV)	0.205	0.474	0.553	0.416	0.828	0.547
Active Excited State	S_{12} (311.99 nm)	S_4 (599.94 nm)	S_3 (521.73 nm)	S_3 (546.55 nm)	S_5 (484.20 nm)	S_2 (554.67 nm)
	T_{21} (308.77 nm)	T_7 (537.14 nm)	T_{12} (401.51 nm)	T_{12} (434.87 nm)	T_8 (463.46 nm)	T_{10} (424.54 nm)

Table 2. The singlet and triplet total energies (in Hartree), the d(Ni···O) bond distances for the singlet and triplet equilibrium geometries (in Å), the singlet-triplet energy gap (in eV) and the first active excited state for both singlet and triplet vertical electronic excitations in the case of the six chosen molecular complexes.

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