Supporting Information

Ab initio study of the Light-Induced Excited State Spin Trapping in Tetrazole-based Spin Crossover systems

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Validation of the method

The adequate choice of the active space and one-electron basis set are essential to obtain reliable results. Given the rather few *ab initio* studies in this field, we performed a study of the dependence of the equilibrium distances of the LS and HS state (R_e) and the energy difference between the two states (ΔE_{HL}) on the size of the active space and the basis set. In the first place, it is observed that the inclusion of dynamical electron correlation effects with CASPT2 has a dramatic effect: R_e is shortened by 0.15 Å and ΔE_{HL} is lowered by more than 11200 cm^{-1}. Table 1 presents the CASSCF/CASPT2 results for three active spaces and Table 2 for five different basis sets. The minimal active space with 6 electrons in 5 mainly Fe-3d orbitals gives similar results as the second active space where the so-called Fe-3d' orbitals have been added, CAS(6,10). Only when we also add two ligand orbitals of e_g symmetry character, CAS(10,12), we observe significant changes. The introduction of the σ-donation in the active space through ligand-to-metal charge transfer configurations involving the e_g-type orbitals slightly increases the difference between R_e(HS) and R_e(LS), but decreases ΔE_{HL} with more than 3000 cm^{-1}.

The effect of the basis set is resumed in Table 2. Five different basis sets for Fe were tested: basis 1 - (6s, 5p, 4d, 2f); basis 2 - (6s, 5p, 4d, 2f, 1g); basis 3 - (6s, 5p, 4d, 3f, 2g, 1h); basis 4 - (7s, 6p, 5d, 3f, 2g, 1h); basis 5 - (7s, 6p, 5d, 4f, 3g, 2h). The equilibrium distances are not significantly affected by the addition of extra basis functions to basis 1. On the contrary, a rather strong effect is observed for ΔE_{HL}, which decreases from ~2500 cm^{-1} to -220 cm^{-1}, for the largest basis set. A further extension of the basis set on the N atoms in the first coordination sphere of Fe with extra s and p functions does not change the ΔE_{HL} value obtained with basis 5, indicating the convergence of the results with the basis set.

Table 1: Dependence of the CASSCF and CASPT2 estimates of R_e(LS) and R_e(HS) (in Å), and ΔE_{HL} (in cm^{-1}) on the size of the active space (CAS), results are obtained with basis 4 (see text).

	CASSCF			CASPT2		
	R_e(LS)	R_e(HS)	ΔE_{HL}	R_e(LS)	R_e(HS)	ΔE_{HL}
CAS(6,5)	2.155	2.290	18152	1.953	2.152	3743
CAS(6,10)	2.142	2.285	15876	1.964	2.156	4331
CAS(10,12)	2.112	2.279	13279	1.946	2.155	725

Table 2: Dependence of the CASPT2 estimates of R_e(LS) and R_e(HS) (in Å), and ΔE_{HL} (in cm^{-1}) on the basis set. Results are obtained with a CAS(10,12) reference wave function.

Basis	R_e(LS)	R_e(HS)	ΔE_{HL}
1	1.961	2.169	2420
2	1.957	2.165	1936
3	1.947	2.155	806
4	1.946	2.155	725
5	1.943	2.153	-220

Energies and cartesian coordinates of the $Fe^{II}(tz)_6$ complex

CASPT2 energy of $^1A_1$ (LS) at R_e=1.95 Å: -2816.4103869536 au

Coordinates (in Å)

Fe	0.000000	0.000000	0.000000
N	1.950000	0.000000	0.000000
N	-1.950000	0.000000	0.000000
N	0.000000	1.950000	0.000000
N	0.000000	-1.950000	0.000000
N	0.000000	0.000000	1.950000
N	0.000000	0.000000	-1.950000
N	3.993800	0.816700	0.000000
N	-3.993800	-0.816700	0.000000
N	4.044700	-0.529500	0.000000
N	-4.044700	0.529500	0.000000
N	2.731100	1.125900	0.000000
N	-2.731100	-1.125900	0.000000
N	0.000000	3.993800	-0.816700
N	0.000000	-3.993800	0.816700
N	0.000000	4.044700	0.529500
N	0.000000	-4.044700	-0.529500
N	0.000000	2.731100	-1.125900
N	0.000000	-2.731100	1.125900
N	-0.816700	0.000000	3.993800
N	0.816700	0.000000	-3.993800
N	0.529500	0.000000	4.044700
N	-0.529500	0.000000	-4.044700
N	-1.125900	0.000000	2.731100
N	1.125900	0.000000	-2.731100
C	2.789900	-1.012700	0.000000
C	-2.789900	1.012700	0.000000
C	0.000000	2.789900	1.012700
C	0.000000	-2.789900	-1.012700
C	1.012700	0.000000	2.789900
C	-1.012700	0.000000	-2.789900
H	2.535800	-2.057000	0.000000
H	-2.535800	2.057000	0.000000
H	4.935900	-1.000700	0.000000
H	-4.935900	1.000700	0.000000
H	0.000000	2.535800	2.057000
H	0.000000	-2.535800	-2.057000
H	0.000000	4.935900	1.000700
H	0.000000	-4.935900	-1.000700
H	2.057000	0.000000	2.535800
H	-2.057000	0.000000	-2.535800
H	1.000700	0.000000	4.935900
H	-1.000700	0.000000	-4.935900

CASPT2 energy of $^5T_2$ (HS) at R_e=2.15 Å: -2816.4093859073 au

Coordinates (in Å)

Fe	0.000000	0.000000	0.000000
N	2.150000	0.000000	0.000000
N	-2.150000	0.000000	0.000000
N	0.000000	2.150000	0.000000
N	0.000000	-2.150000	0.000000
N	0.000000	0.000000	2.150000
N	0.000000	0.000000	-2.150000
N	4.193800	0.816700	0.000000
N	-4.193800	-0.816700	0.000000
N	4.244700	-0.529500	0.000000
N	-4.244700	0.529500	0.000000
N	2.931100	1.125900	0.000000
N	-2.931100	-1.125900	0.000000
N	0.000000	4.193800	-0.816700
N	0.000000	-4.193800	0.816700
N	0.000000	4.244700	0.529500
N	0.000000	-4.244700	-0.529500
N	0.000000	2.931100	-1.125900
N	0.000000	-2.931100	1.125900
N	-0.816700	0.000000	4.193800
N	0.816700	0.000000	-4.193800
N	0.529500	0.000000	4.244700
N	-0.529500	0.000000	-4.244700
N	-1.125900	0.000000	2.931100
N	1.125900	0.000000	-2.931100
C	2.989900	-1.012700	0.000000
C	-2.989900	1.012700	0.000000
C	0.000000	2.989900	1.012700
C	0.000000	-2.989900	-1.012700
C	1.012700	0.000000	2.989900
C	-1.012700	0.000000	-2.989900
H	2.735800	-2.057000	0.000000
H	-2.735800	2.057000	0.000000
H	5.135900	-1.000700	0.000000
H	-5.135900	1.000700	0.000000
H	0.000000	2.735800	2.057000
H	0.000000	-2.735800	-2.057000
H	0.000000	5.135900	1.000700
H	0.000000	-5.135900	-1.000700
H	2.057000	0.000000	2.735800
H	-2.057000	0.000000	-2.735800
H	1.000700	0.000000	5.135900
H	-1.000700	0.000000	-5.135900

Energies and cartesian coordinates of the $Co^{III}(tz)_6$ complex

CASPT2 energy of $^1A_1$ (LS) at R_e=1.90 Å: -2936.5343166174 au

Coordinates (in Å)

Co	0.000000	0.000000	0.000000
N	1.900000	0.000000	0.000000
N	-1.900000	0.000000	0.000000
N	0.000000	1.900000	0.000000
N	0.000000	-1.900000	0.000000
N	0.000000	0.000000	1.900000
N	0.000000	0.000000	-1.900000
N	3.943800	0.816700	0.000000
N	-3.943800	-0.816700	0.000000
N	3.994700	-0.529500	0.000000
N	-3.994700	0.529500	0.000000
N	2.681100	1.125900	0.000000
N	-2.681100	-1.125900	0.000000
N	0.000000	3.943800	-0.816700
N	0.000000	-3.943800	0.816700
N	0.000000	3.994700	0.529500
N	0.000000	-3.994700	-0.529500
N	0.000000	2.681100	-1.125900
N	0.000000	-2.681100	1.125900
N	-0.816700	0.000000	3.943800
N	0.816700	0.000000	-3.943800
N	0.529500	0.000000	3.994700
N	-0.529500	0.000000	-3.994700
N	-1.125900	0.000000	2.681100
N	1.125900	0.000000	-2.681100
C	2.739900	-1.012700	0.000000
C	-2.739900	1.012700	0.000000
C	0.000000	2.739900	1.012700
C	0.000000	-2.739900	-1.012700
C	1.012700	0.000000	2.739900
C	-1.012700	0.000000	-2.739900
H	2.485800	-2.057000	0.000000
H	-2.485800	2.057000	0.000000
H	4.885900	-1.000700	0.000000
H	-4.885900	1.000700	0.000000
H	0.000000	2.485800	2.057000
H	0.000000	-2.485800	-2.057000
H	0.000000	4.885900	1.000700
H	0.000000	-4.885900	-1.000700
H	2.057000	0.000000	2.485800
H	-2.057000	0.000000	-2.485800
H	1.000700	0.000000	4.885900
H	-1.000700	0.000000	-4.885900

CASPT2 energy of $^5T_2$ (HS) at R_e=2.05 Å: -2936.4643481136 au

Coordinates (in Å)

Co	0.000000	0.000000	0.000000
N	2.050000	0.000000	0.000000
N	-2.050000	0.000000	0.000000
N	0.000000	2.050000	0.000000
N	0.000000	-2.050000	0.000000
N	0.000000	0.000000	2.050000
N	0.000000	0.000000	-2.050000
N	4.093800	0.816700	0.000000
N	-4.093800	-0.816700	0.000000
N	4.144700	-0.529500	0.000000
N	-4.144700	0.529500	0.000000
N	2.831100	1.125900	0.000000
N	-2.831100	-1.125900	0.000000
N	0.000000	4.093800	-0.816700
N	0.000000	-4.093800	0.816700
N	0.000000	4.144700	0.529500
N	0.000000	-4.144700	-0.529500
N	0.000000	2.831100	-1.125900
N	0.000000	-2.831100	1.125900
N	-0.816700	0.000000	4.093800
N	0.816700	0.000000	-4.093800
N	0.529500	0.000000	4.144700
N	-0.529500	0.000000	-4.144700
N	-1.125900	0.000000	2.831100
N	1.125900	0.000000	-2.831100
C	2.889900	-1.012700	0.000000
C	-2.889900	1.012700	0.000000
C	0.000000	2.889900	1.012700
C	0.000000	-2.889900	-1.012700
C	1.012700	0.000000	2.889900
C	-1.012700	0.000000	-2.889900
H	2.635800	-2.057000	0.000000
H	-2.635800	2.057000	0.000000
H	5.035900	-1.000700	0.000000
H	-5.035900	1.000700	0.000000
H	0.000000	2.635800	2.057000
H	0.000000	-2.635800	-2.057000
H	0.000000	5.035900	1.000700
H	0.000000	-5.035900	-1.000700
H	2.057000	0.000000	2.635800
H	-2.057000	0.000000	-2.635800
H	1.000700	0.000000	5.035900
H	-1.000700	0.000000	-5.035900

Energies and cartesian coordinates of the $Fe^{III}(tz)_6$ complex

CASPT2 energy of $^2T_2$ (LS) at R_e=1.94 Å: -2815.9113257563 au

Coordinates (in Å)

Fe	0.000000	0.000000	0.000000
N	1.940000	0.000000	0.000000
N	-1.940000	0.000000	0.000000
N	0.000000	1.940000	0.000000
N	0.000000	-1.940000	0.000000
N	0.000000	0.000000	1.940000
N	0.000000	0.000000	-1.940000
N	3.983800	0.816700	0.000000
N	-3.983800	-0.816700	0.000000
N	4.034700	-0.529500	0.000000
N	-4.034700	0.529500	0.000000
N	2.721100	1.125900	0.000000
N	-2.721100	-1.125900	0.000000
N	0.000000	3.983800	-0.816700
N	0.000000	-3.983800	0.816700
N	0.000000	4.034700	0.529500
N	0.000000	-4.034700	-0.529500
N	0.000000	2.721100	-1.125900
N	0.000000	-2.721100	1.125900
N	-0.816700	0.000000	3.983800
N	0.816700	0.000000	-3.983800
N	0.529500	0.000000	4.034700
N	-0.529500	0.000000	-4.034700
N	-1.125900	0.000000	2.721100
N	1.125900	0.000000	-2.721100
C	2.779900	-1.012700	0.000000
C	-2.779900	1.012700	0.000000
C	0.000000	2.779900	1.012700
C	0.000000	-2.779900	-1.012700
C	1.012700	0.000000	2.779900
C	-1.012700	0.000000	-2.779900
H	2.525800	-2.057000	0.000000
H	-2.525800	2.057000	0.000000
H	4.925900	-1.000700	0.000000
H	-4.925900	1.000700	0.000000
H	0.000000	2.525800	2.057000
H	0.000000	-2.525800	-2.057000
H	0.000000	4.925900	1.000700
H	0.000000	-4.925900	-1.000700
H	2.057000	0.000000	2.525800
H	-2.057000	0.000000	-2.525800
H	1.000700	0.000000	4.925900
H	-1.000700	0.000000	-4.925900

CASPT2 energy of $^6A_1$ (HS) at R_e=2.08 Å: -2815.9179705435 au

Coordinates (in Å)

Fe	0.000000	0.000000	0.000000
N	2.080000	0.000000	0.000000
N	-2.080000	0.000000	0.000000
N	0.000000	2.080000	0.000000
N	0.000000	-2.080000	0.000000
N	0.000000	0.000000	2.080000
N	0.000000	0.000000	-2.080000
N	4.123800	0.816700	0.000000
N	-4.123800	-0.816700	0.000000
N	4.174700	-0.529500	0.000000
N	-4.174700	0.529500	0.000000
N	2.861100	1.125900	0.000000
N	-2.861100	-1.125900	0.000000
N	0.000000	4.123800	-0.816700
N	0.000000	-4.123800	0.816700
N	0.000000	4.174700	0.529500
N	0.000000	-4.174700	-0.529500
N	0.000000	2.861100	-1.125900
N	0.000000	-2.861100	1.125900
N	-0.816700	0.000000	4.123800
N	0.816700	0.000000	-4.123800
N	0.529500	0.000000	4.174700
N	-0.529500	0.000000	-4.174700
N	-1.125900	0.000000	2.861100
N	1.125900	0.000000	-2.861100
C	2.919900	-1.012700	0.000000
C	-2.919900	1.012700	0.000000
C	0.000000	2.919900	1.012700
C	0.000000	-2.919900	-1.012700
C	1.012700	0.000000	2.919900
C	-1.012700	0.000000	-2.919900
H	2.665800	-2.057000	0.000000
H	-2.665800	2.057000	0.000000
H	5.065900	-1.000700	0.000000
H	-5.065900	1.000700	0.000000
H	0.000000	2.665800	2.057000
H	0.000000	-2.665800	-2.057000
H	0.000000	5.065900	1.000700
H	0.000000	-5.065900	-1.000700
H	2.057000	0.000000	2.665800
H	-2.057000	0.000000	-2.665800
H	1.000700	0.000000	5.065900
H	-1.000700	0.000000	-5.065900

Energies and cartesian coordinates of the $Co^{II}(tz)_6$ complex

CASPT2 energy of $^2A_1$ (LS) at R_{eq}=1.93 Å and R_{ax}=2.14 Å: -2937.0000473777 au

Coordinates (in Å)

Co	0.000000	0.000000	0.000000
N	1.930000	0.000000	0.000000
N	-1.930000	0.000000	0.000000
N	0.000000	1.930000	0.000000
N	0.000000	-1.930000	0.000000
N	0.000000	0.000000	2.140000
N	0.000000	0.000000	-2.140000
N	3.973800	0.816700	0.000000
N	-3.973800	-0.816700	0.000000
N	4.024700	-0.529500	0.000000
N	-4.024700	0.529500	0.000000
N	2.711100	1.125900	0.000000
N	-2.711100	-1.125900	0.000000
N	0.000000	3.973800	-0.816700
N	0.000000	-3.973800	0.816700
N	0.000000	4.024700	0.529500
N	0.000000	-4.024700	-0.529500
N	0.000000	2.711100	-1.125900
N	0.000000	-2.711100	1.125900
N	-0.816700	0.000000	4.183800
N	0.816700	0.000000	-4.183800
N	0.529500	0.000000	4.234700
N	-0.529500	0.000000	-4.234700
N	-1.125900	0.000000	2.921100
N	1.125900	0.000000	-2.921100
C	2.769900	-1.012700	0.000000
C	-2.769900	1.012700	0.000000
C	0.000000	2.769900	1.012700
C	0.000000	-2.769900	-1.012700
C	1.012700	0.000000	2.979900
C	-1.012700	0.000000	-2.979900
H	2.515800	-2.057000	0.000000
H	-2.515800	2.057000	0.000000
H	4.915900	-1.000700	0.000000
H	-4.915900	1.000700	0.000000
H	0.000000	2.515800	2.057000
H	0.000000	-2.515800	-2.057000
H	0.000000	4.915900	1.000700
H	0.000000	-4.915900	-1.000700
H	2.057000	0.000000	2.725800
H	-2.057000	0.000000	-2.725800
H	1.000700	0.000000	5.125900
H	-1.000700	0.000000	-5.125900

CASPT2 energy of $^4T_1$ (HS) at R_e=2.10 Å: -2937.0050205836 au

Coordinates (in Å)

Co	0.000000	0.000000	0.000000
N	2.100000	0.000000	0.000000
N	-2.100000	0.000000	0.000000
N	0.000000	2.100000	0.000000
N	0.000000	-2.100000	0.000000
N	0.000000	0.000000	2.100000
N	0.000000	0.000000	-2.100000
N	4.143800	0.816700	0.000000
N	-4.143800	-0.816700	0.000000
N	4.194700	-0.529500	0.000000
N	-4.194700	0.529500	0.000000
N	2.881100	1.125900	0.000000
N	-2.881100	-1.125900	0.000000
N	0.000000	4.143800	-0.816700
N	0.000000	-4.143800	0.816700
N	0.000000	4.194700	0.529500
N	0.000000	-4.194700	-0.529500
N	0.000000	2.881100	-1.125900
N	0.000000	-2.881100	1.125900
N	-0.816700	0.000000	4.143800
N	0.816700	0.000000	-4.143800
N	0.529500	0.000000	4.194700
N	-0.529500	0.000000	-4.194700
N	-1.125900	0.000000	2.881100
N	1.125900	0.000000	-2.881100
C	2.939900	-1.012700	0.000000
C	-2.939900	1.012700	0.000000
C	0.000000	2.939900	1.012700
C	0.000000	-2.939900	-1.012700
C	1.012700	0.000000	2.939900
C	-1.012700	0.000000	-2.939900
H	2.685800	-2.057000	0.000000
H	-2.685800	2.057000	0.000000
H	5.085900	-1.000700	0.000000
H	-5.085900	1.000700	0.000000
H	0.000000	2.685800	2.057000
H	0.000000	-2.685800	-2.057000
H	0.000000	5.085900	1.000700
H	0.000000	-5.085900	-1.000700
H	2.057000	0.000000	2.685800
H	-2.057000	0.000000	-2.685800
H	1.000700	0.000000	5.085900
H	-1.000700	0.000000	-5.085900

Energies and cartesian coordinates of the $Fe^{II}(tz)_6$ complex at the crossing in the $e_g(\varepsilon)$ mode around 4.8a

CASPT2 energy of $^1T_1$ at R_{eq}=1.988 Å and R_{ax}=1.844 Å: -2816.3302119516 au

CASPT2 energy of $^3T_2(2)$ at R_{eq}=1.988 Å and R_{ax}=1.844 Å: -2816.3301922292 au

Coordinates (in Å)

Fe	0.000000	0.000000	0.000000
N	1.844000	0.000000	0.000000
N	-1.844000	0.000000	0.000000
N	0.000000	1.988000	0.000000
N	0.000000	-1.988000	0.000000
N	0.000000	0.000000	1.988000
N	0.000000	0.000000	-1.988000
N	3.887800	0.816700	0.000000
N	-3.887800	-0.816700	0.000000
N	3.938700	-0.529500	0.000000
N	-3.938700	0.529500	0.000000
N	2.625100	1.125900	0.000000
N	-2.625100	-1.125900	0.000000
N	0.000000	4.031800	-0.816700
N	0.000000	-4.031800	0.816700
N	0.000000	4.082700	0.529500
N	0.000000	-4.082700	-0.529500
N	0.000000	2.769100	-1.125900
N	0.000000	-2.769100	1.125900
N	-0.816700	0.000000	4.031800
N	0.816700	0.000000	-4.031800
N	0.529500	0.000000	4.082700
N	-0.529500	0.000000	-4.082700
N	-1.125900	0.000000	2.769100
N	1.125900	0.000000	-2.769100
C	2.683900	-1.012700	0.000000
C	-2.683900	1.012700	0.000000
C	0.000000	2.827900	1.012700
C	0.000000	-2.827900	-1.012700
C	1.012700	0.000000	2.827900
C	-1.012700	0.000000	-2.827900
H	2.429800	-2.057000	0.000000
H	-2.429800	2.057000	0.000000
H	4.829900	-1.000700	0.000000
H	-4.829900	1.000700	0.000000
H	0.000000	2.573800	2.057000
H	0.000000	-2.573800	-2.057000
H	0.000000	4.973900	1.000700
H	0.000000	-4.973900	-1.000700
H	2.057000	0.000000	2.573800
H	-2.057000	0.000000	-2.573800
H	1.000700	0.000000	4.973900
H	-1.000700	0.000000	-4.973900