

DFT Modeling of Singlet-Triplet Spin Transitions in Ni(II)-based Macrocyclic-ligand Supramolecular Complexes

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Outline

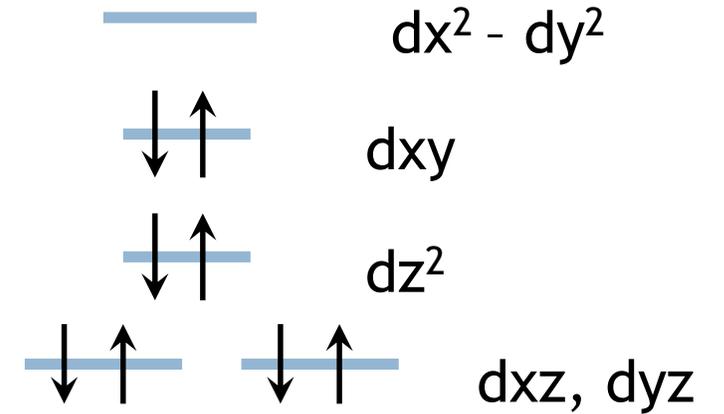
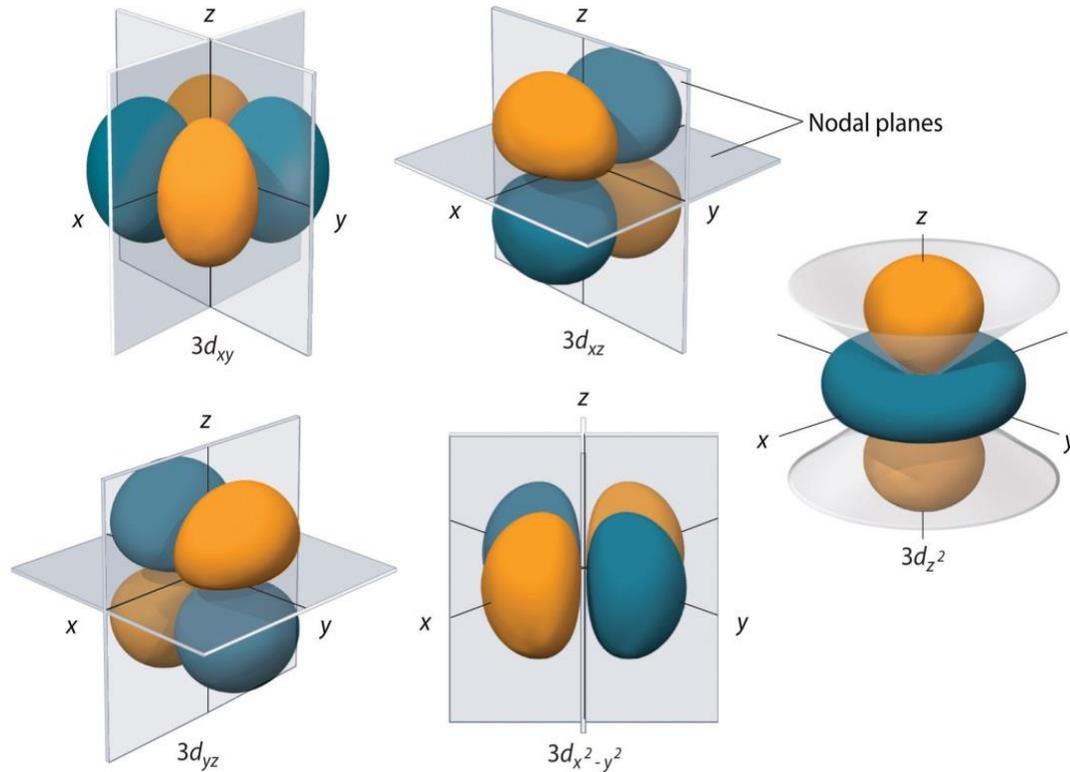
- Spin transitions in organometallics
- Theoretical description using first principle methods
- Spin transitions in large molecular complexes
- The role of different XC functionals



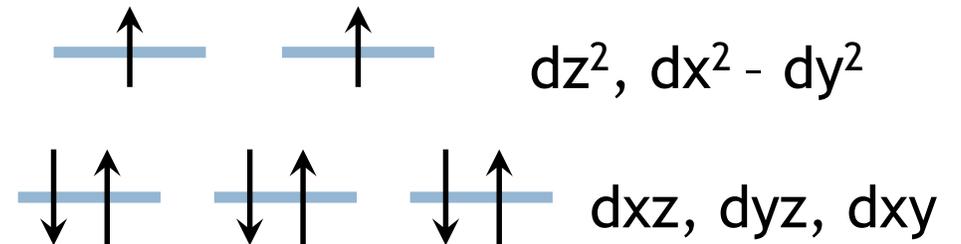
Spin transitions in organometallics

“Square-planar” coordination of the Ni(II) in singlet spin configuration

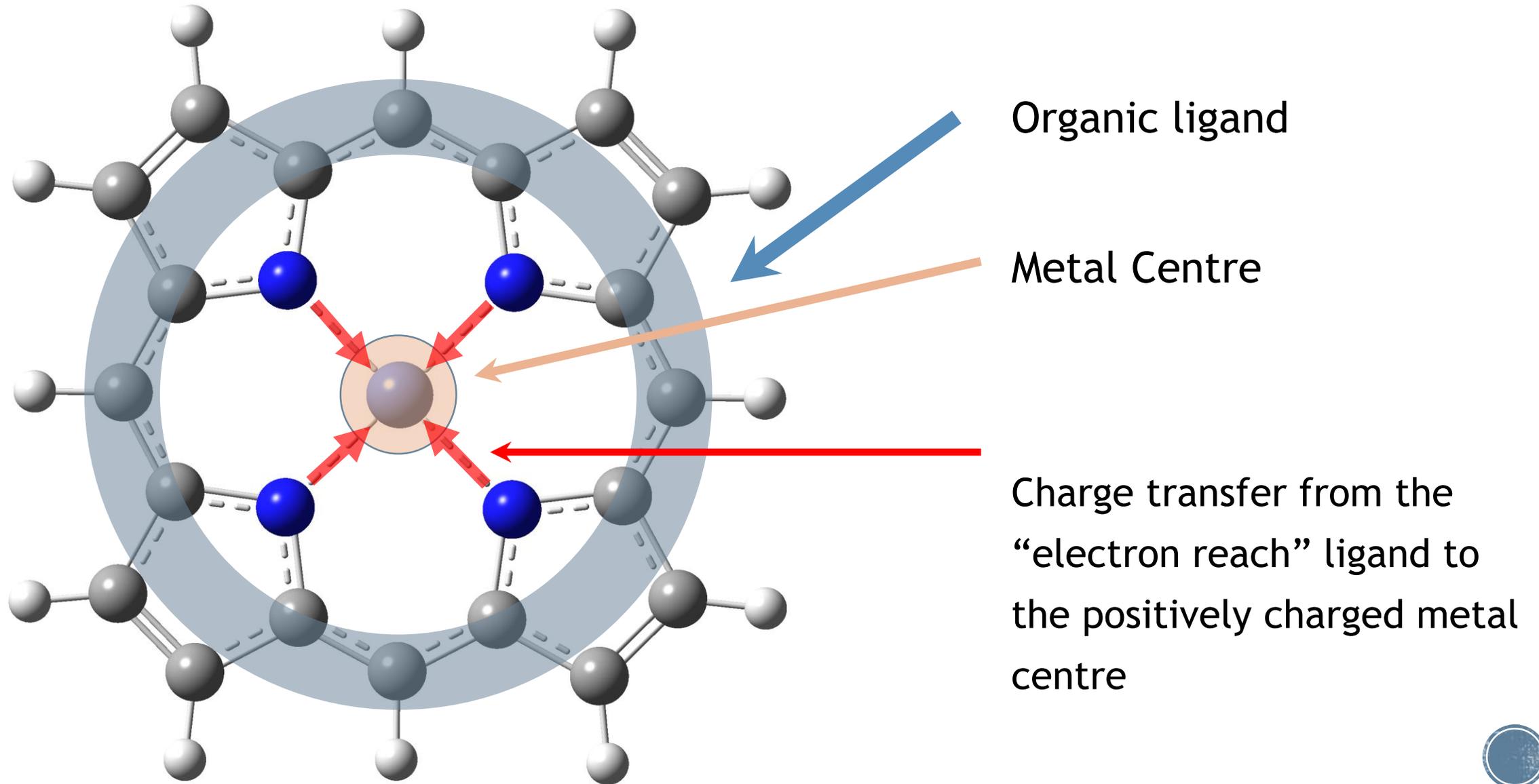
3d orbitals of Ni(II)



“Octahedral” coordination of the Ni(II) in triplet spin configuration



Spin transitions in organometallics



Theoretical description using first principle methods

- Strong multireference character of the electronic states due to the close-lying *d* orbitals and charge transfer effects.

→ Needs multireference methods: MRCF, MRCI, etc.

Maximum: (20,10+5) - 20 electron with 10 occupied and 5 virtual orbitals

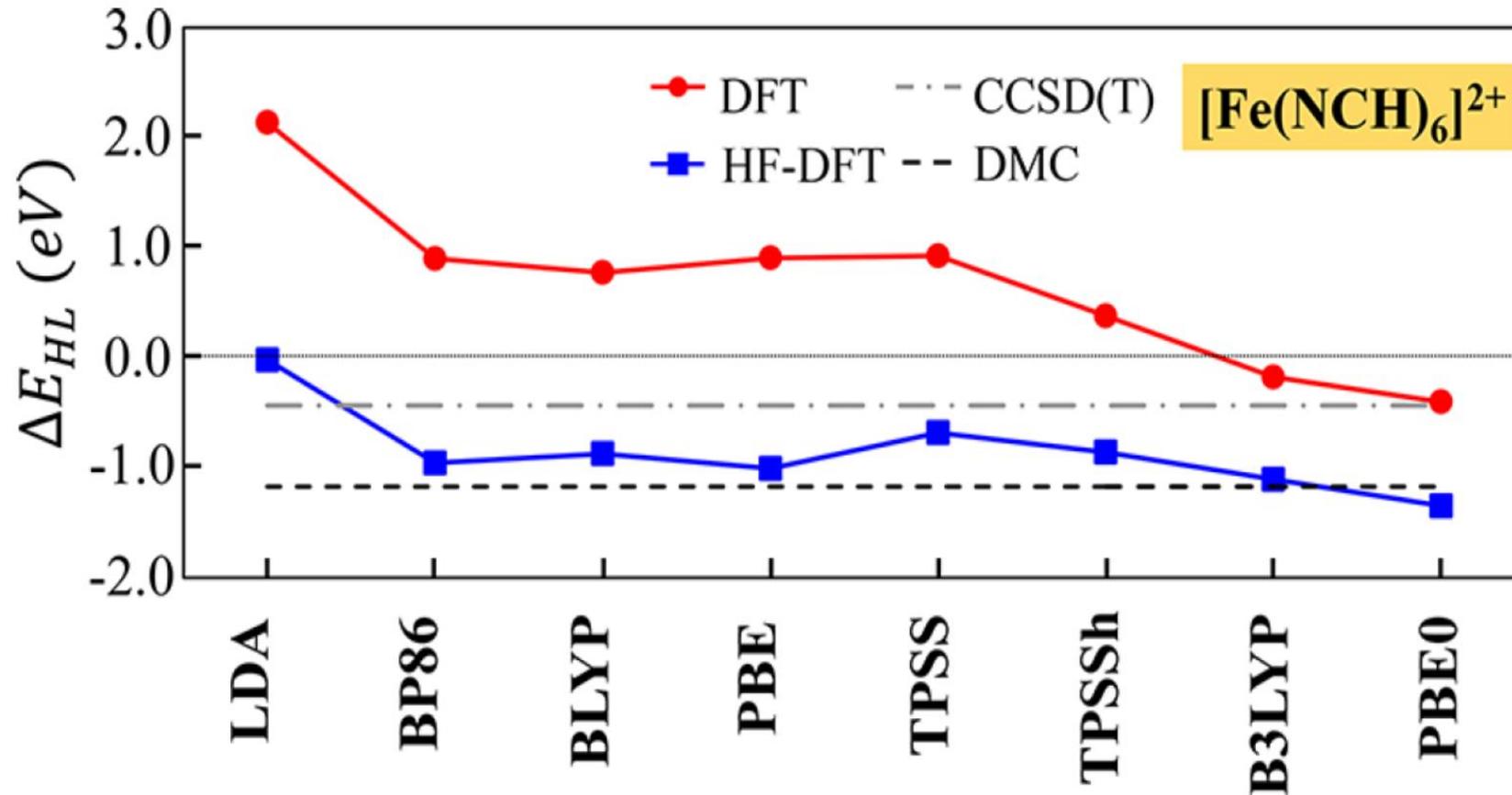
Ni-porphyrin: 8 *d* e of Ni + 8 lone pair e of N-s + 4 x 4p e of pyrrole =
32 e in the active space (16 occupied orbitals)

→ Active space: (32,22)

- Dynamic electron correlation due to the pair (or higher) correlation between the electrons.



Question: Which one?

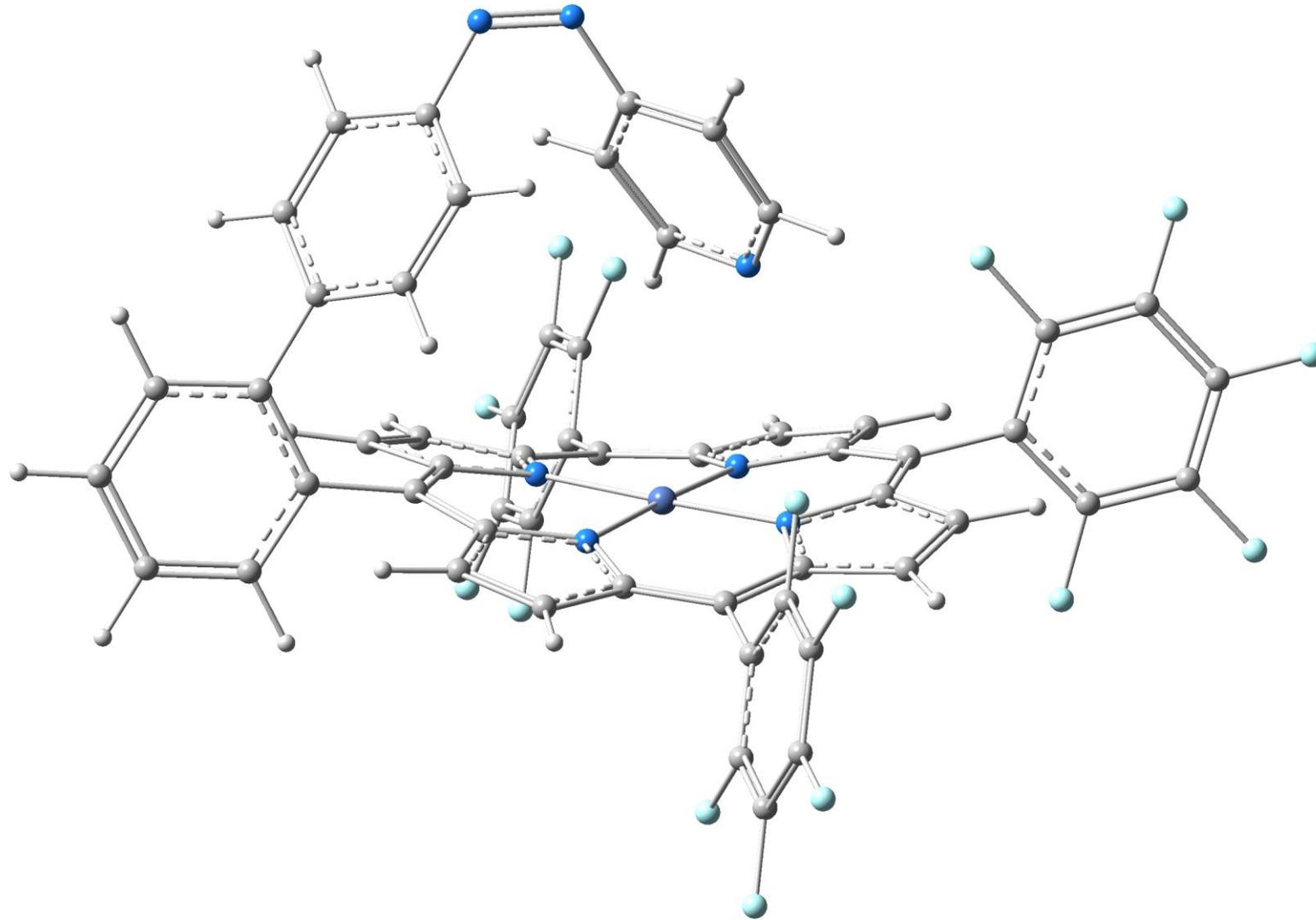


Song et al.
J. Chem. Theory
Comput.
2018, 14, 2304–2311

DMC - Diffusion Monte-Carlo method



Spin transitions in large molecular complexes



Ni-tetrakis(pentafluorophenyl)-
porphyrin functionalized with
a single phenazopyridine arm
(NiTPP-PAPy)



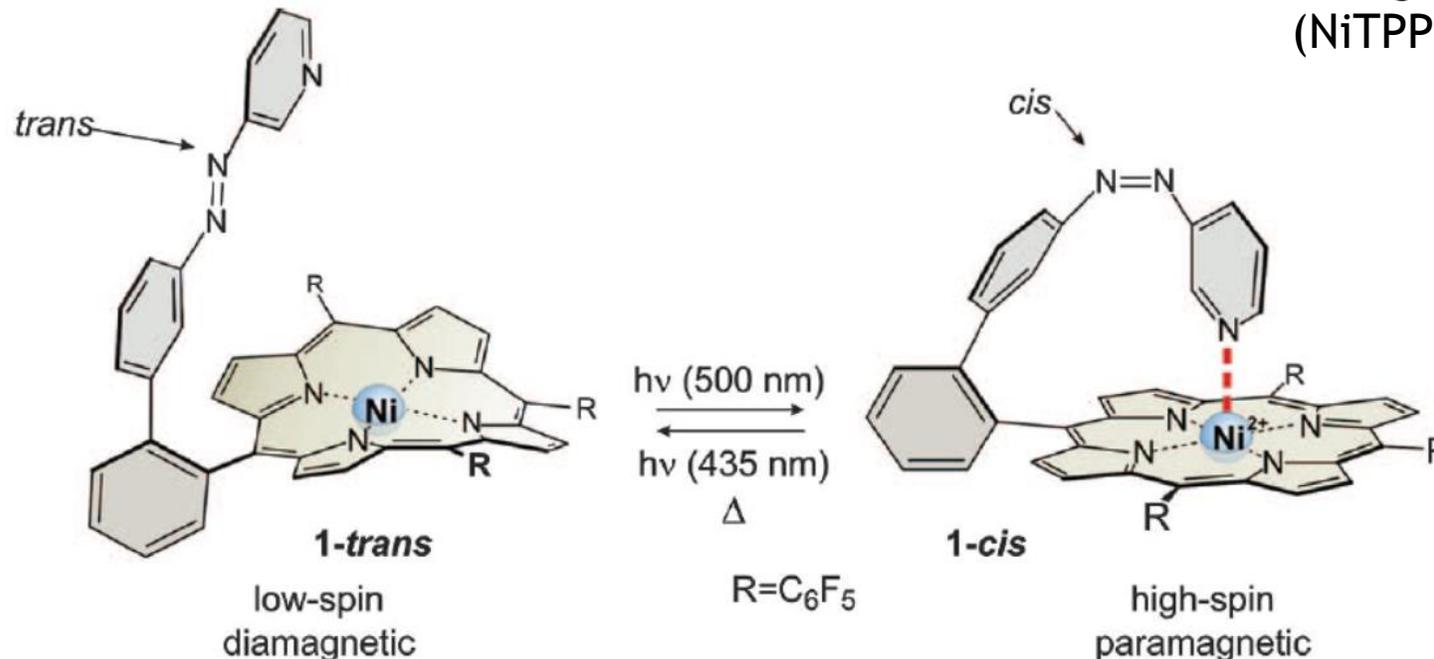
Spin transitions in large molecular complexes

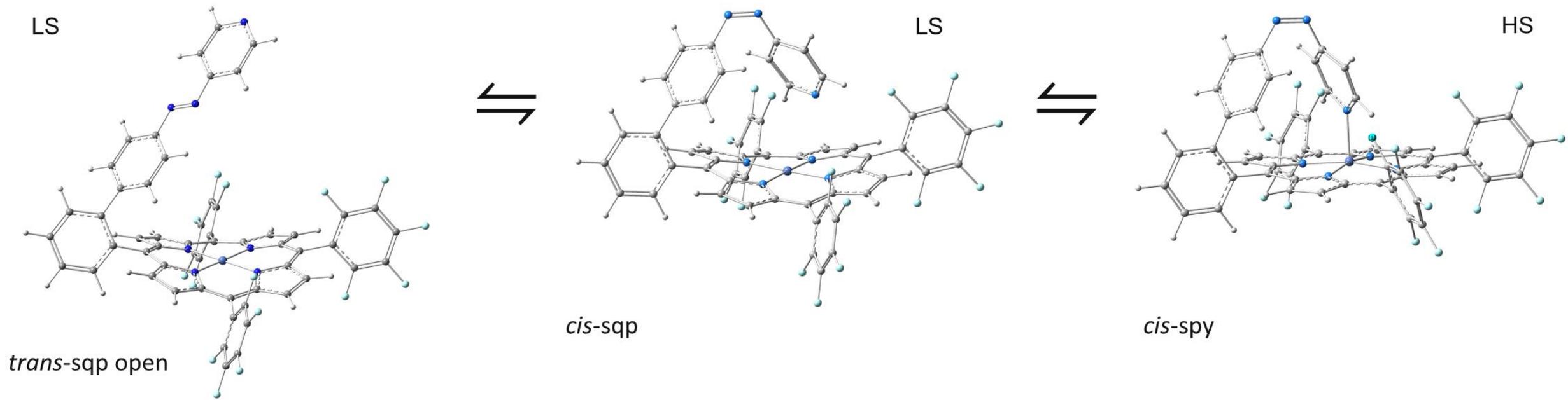
Light-induced excited state spin trapping (LIESST)

The first experiment was done in 1985 by Decurtins et al in solid phase structures based on Fe(II) 53-61 K temperature.

In liquid phase, at room temperature (*Science*, 2011, 331, 445):

Ni-tetrakis(pentafluorophenyl)-porphyrin functionalized with a single phenazopyridine arm (NiTPP-PAPy)





Adiabatic energy gap: $\Delta E = E(\text{LS}) - E(\text{HS})$

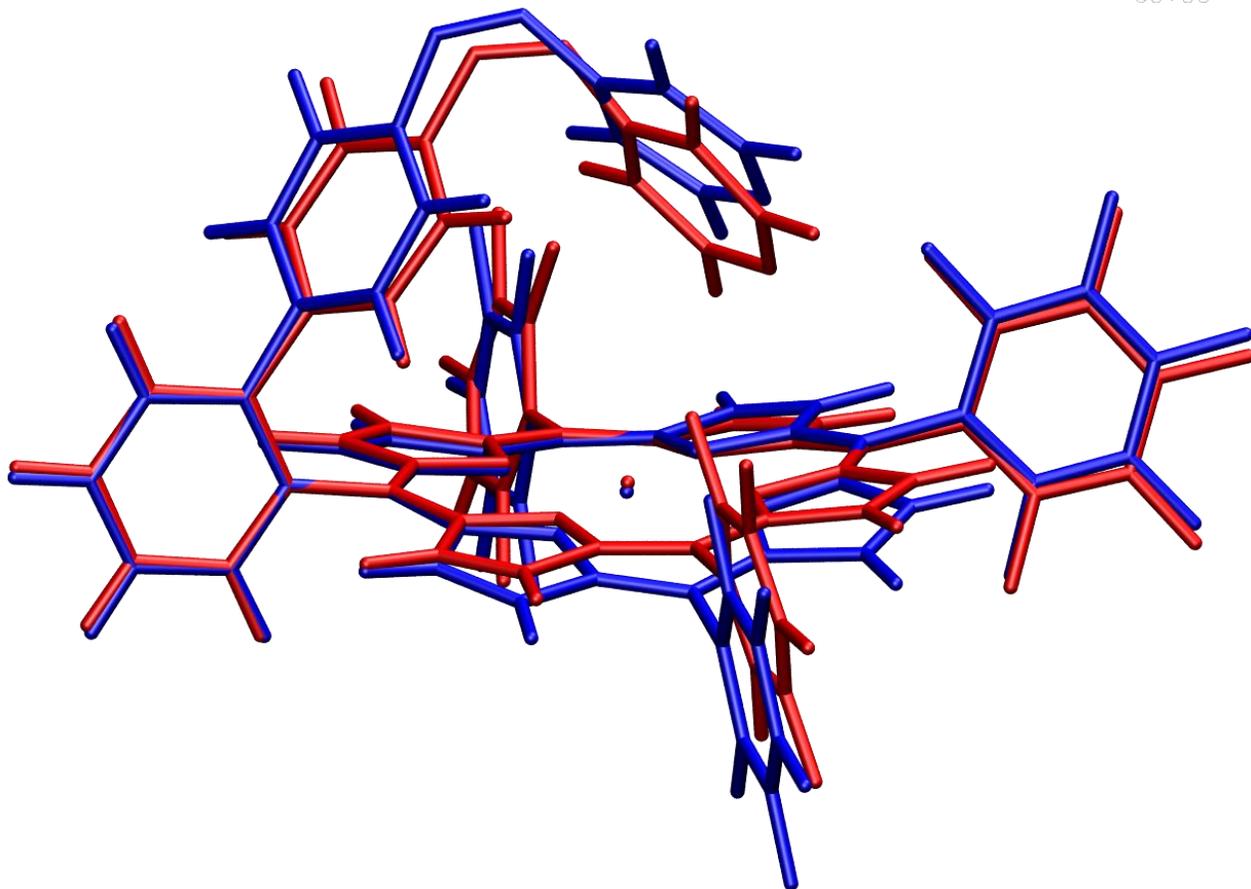


The role of different XC functionals

Values	XC Functionals					
	B3LYP	CAM-B3LYP	CAM-B3LYP-D	M06-L (0%)	M06 (27%)	M06-2X (54%)
E_{singlet} (H)	-5498.61471573	-5497.04107263	-5497.20375561	-5498.03480956	-5496.26727825	-5497.12149327
E_{triplet} (H)	-5498.61345808	-5497.04602376	-5497.21386662	-5498.04036581	-5496.26884836	-5497.15024947
Gap _{S-T} (eV)	0.034	-0.134	-0.275	-0.151	-0.043	-0.782
(Ni – N) _S (Å)	4.982	4.456	3.597	3.415	3.723	2.981
(Ni – N) _T (Å)	2.1220	2.113	2.089	2.107	2.097	2.144
Values	XC Functionals					
	M11-L	M11	MN12-L	MN12-SX	N12	N12-SX
E_{singlet} (H)	-5497.71462536	-5496.80021728	-5495.28011221	-5495.77722521	-5499.22857347	-5496.39404762
E_{triplet} (H)	-5497.72473013	-5496.81505495	-5495.25499857	-5495.76889684	-5499.20143900	-5496.38599753
Gap _{S-T} (eV)	-0.275	-0.403	0.683	0.227	0.738	0.219
(Ni – N) _S (Å)	4.206	2.963	3.288	3.321	5.718	4.565
(Ni – N) _T (Å)	2.056	2.122	2.028	2.089	2.048	2.105



B₃LYP vs. B₃LYP-D



Values	B3LYP	B3LYP-D
E _{singlet} (H)	-5498.61471573	-5498.92166059
E _{triplet} (H)	-5498.61345808	-5498.92907580
Gap _{S-T} (eV)	0.034	-0.202
(Ni - N) _S (Å)	4.982	3.918
(Ni - N) _T (Å)	2.1220	2.093

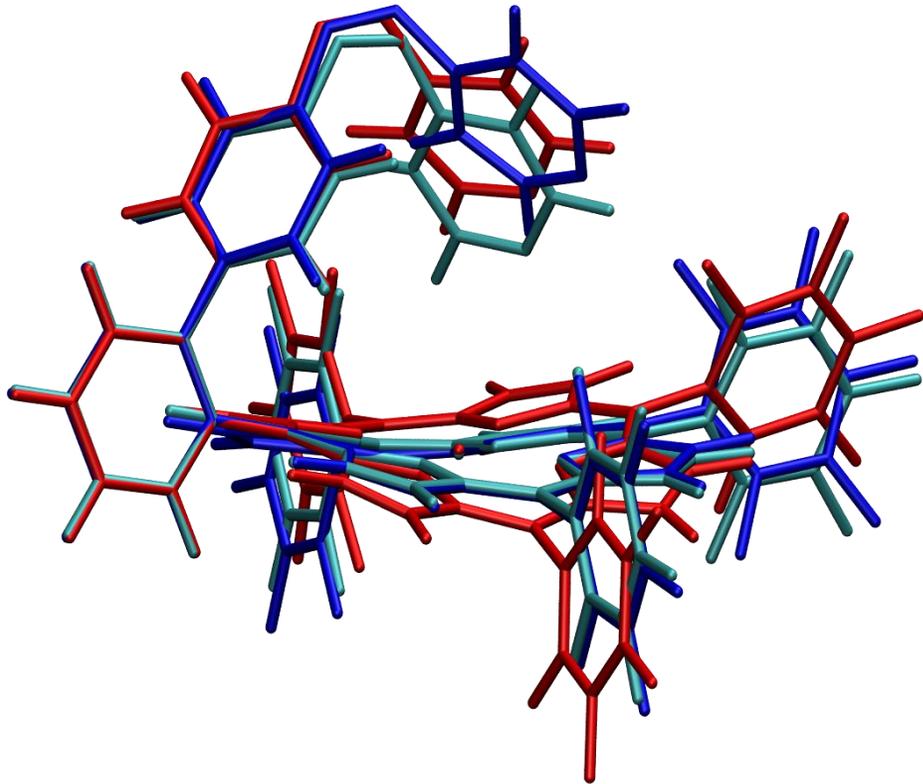
B3LYP:

- Exchange: Becke's 1988 functional, with Slater exchange + Hartree-Fock exchange (20%)
- Correlation: Non-local: LYP and local: VWN
- Dispersion: GD3BJ - D3 version of Grimme's dispersion with Becke-Johnson damping

Dispersion effects: \approx 0.2 eV lower energy and 1 Å shorter Ni - N bond distance



B₃LYP vs. CAM-B₃LYP vs. CAM-B₃LYP-D



Values	B ₃ LYP	CAM-B ₃ LYP	CAM-B ₃ LYP-D
E _{singlet} (H)	-5498.61471573	-5497.04107263	-5497.20375561
E _{triplet} (H)	-5498.61345808	-5497.04602376	-5497.21386662
Gap _{S-T} (eV)	0.034	-0.134	-0.275
(Ni - N) _S (Å)	4.982	4.456	3.597
(Ni - N) _T (Å)	2.1220	2.113	2.089

CAM-B₃LYP:

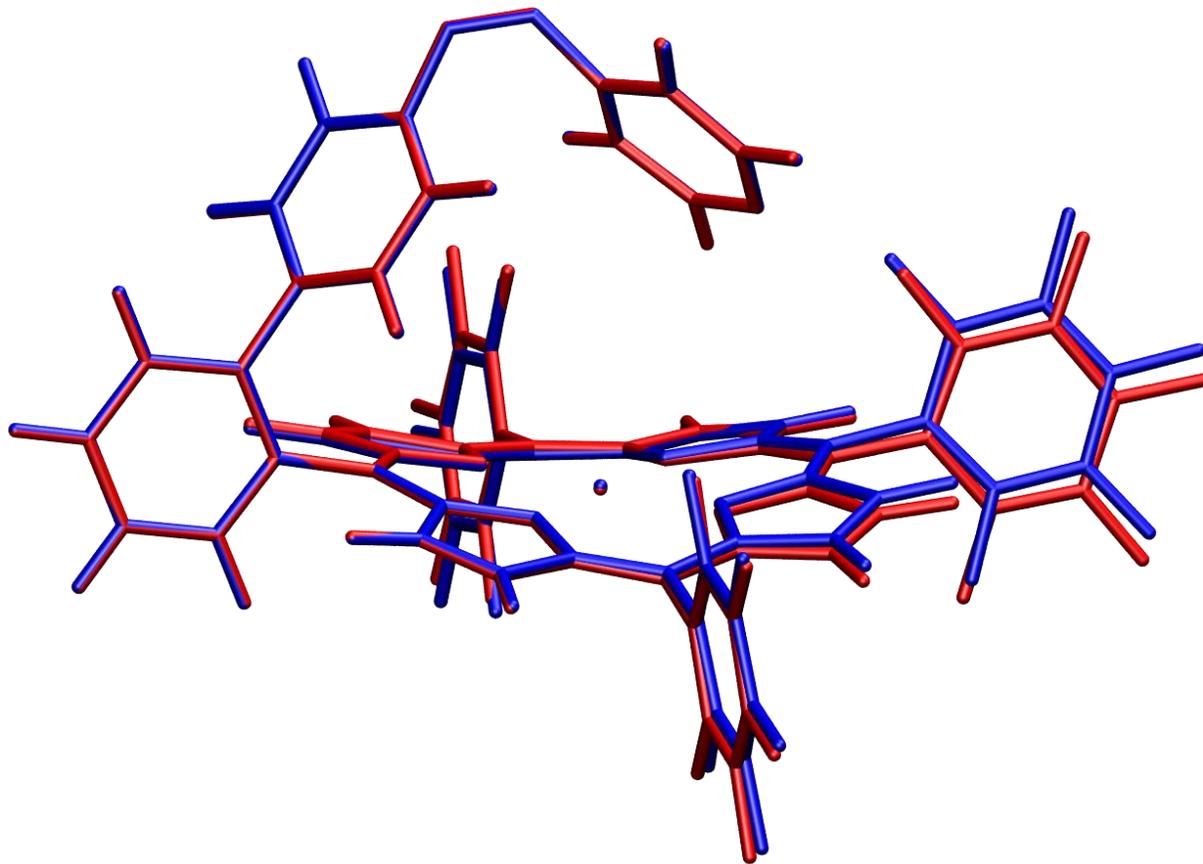
- Exchange: Becke's 1988 functional, with Slater exchange + Hartree-Fock exchange (from 20% to 60% at long range)

HF exchange : ≈ 0.16 eV lower energy and ≈ 0.5 Å shorter Ni - N bond distance

HF exchange + Dispersion effects: ≈ 0.3 eV lower energy and 1.5 Å shorter Ni - N bond distance



B₃LYP vs. B₃LYP*



Values	B3LYP	B3LYP*
$E_{\text{singlet}} \text{ (H)}$	-5498.61471573	-5496.18990398
$E_{\text{triplet}} \text{ (H)}$	-5498.61345808	-5496.18318044
$\text{Gap}_{\text{S-T}} \text{ (eV)}$	0.034	0.183
$(\text{Ni} - \text{N})_{\text{S}} \text{ (Å)}$	4.982	4.932
$(\text{Ni} - \text{N})_{\text{T}} \text{ (Å)}$	2.1220	2.093

B3LYP*:

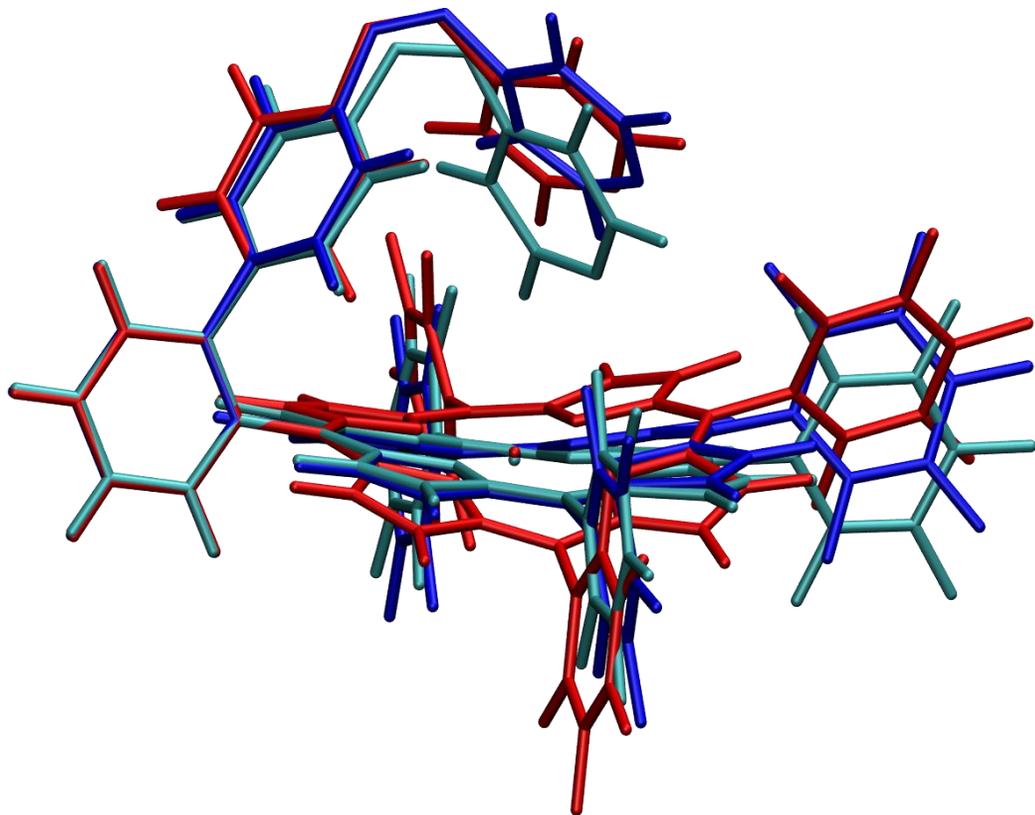
- Exchange: Becke's 1988 functional, with Slater exchange + Hartree-Fock exchange (15%)

Assertion and validation of the performance of the B3LYP* functional for the first transition metal row and the G2 test set
[Oliver Salomon](#), [Markus Reiher](#), and [Bernd Artur Hess](#)
The Journal of Chemical Physics 117, 4729 (2002);

5% lower HF exchange: $\approx 0.15 \text{ eV}$ higher energy but **NO Ni - N bond distance changes**



B3LYP vs. HSE06 vs. ω B97XD



Values	B3LYP	HSE06	ω B97XD
E_{singlet} (H)	-5498.61471573	-5494.43471857	-5497.36011055
E_{triplet} (H)	-5498.61345808	-5494.44298836	-5497.37234510
Gap _{S-T} (eV)	0.034	-0.225	-0.333
(Ni – N) _S (Å)	4.982	4.611	3.295
(Ni – N) _T (Å)	2.1220	2.104	2.101

HSE06:

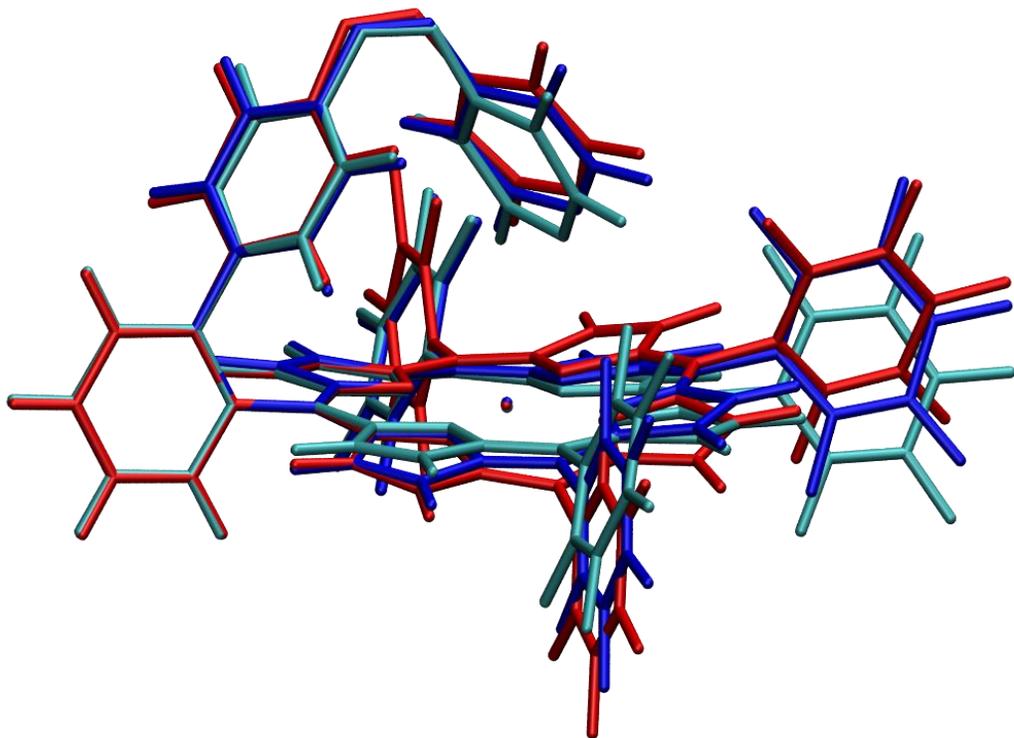
- Exchange: short range - mixed PBE and HX exchange; long range - only PBE exchange

ω B97XD

- Becke's 97 DFT exchange + Hartree-Fock exchange (from 22% to 44% at long range)
- empirical dispersion correction



Mo6-L vs. Mo6 vs. Mo6-2X



Values	M06-L	M06 (27%)	M06-2X (54%)
$E_{\text{singlet}} \text{ (H)}$	-5498.03480956	-5496.26727825	-5497.12149327
$E_{\text{triplet}} \text{ (H)}$	-5498.04036581	-5496.26884836	-5497.15024947
$\text{Gap}_{\text{S-T}} \text{ (eV)}$	-0.151	-0.043	-0.782
$(\text{Ni} - \text{N})_{\text{S}} \text{ (Å)}$	3.415	3.723	2.981
$(\text{Ni} - \text{N})_{\text{T}} \text{ (Å)}$	2.107	2.097	2.144

M06-L:

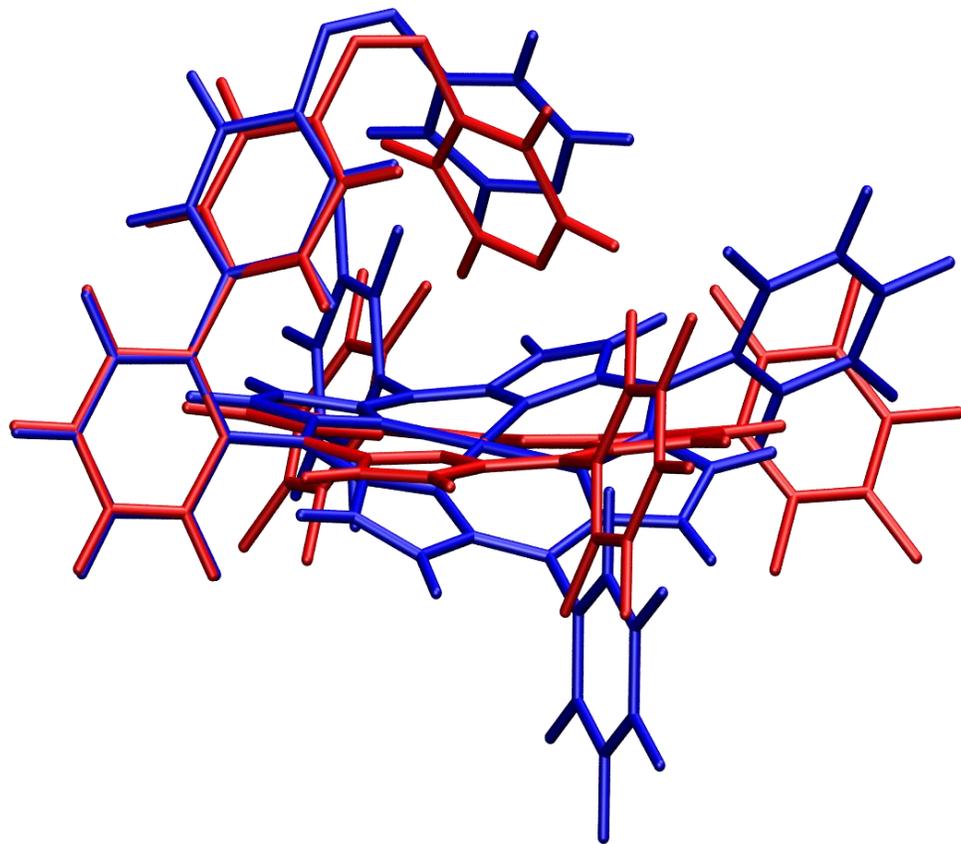
- Exchange: Mixture of PBE and LSDA
- Correlation: VSXC and treat the opposite-spin and parallel-spin correlation differently

M06 with 27% HF exchange: - decreases the Gap and enlarge the Ni - N bond distance

M06 with 54% HF exchange: - increases the Gap and shorten the Ni - N bond distance



M11-L vs. M11



Values	M11-L	M11
$E_{\text{singlet}} \text{ (H)}$	-5497.71462536	-5496.80021728
$E_{\text{triplet}} \text{ (H)}$	-5497.72473013	-5496.81505495
$\text{Gap}_{\text{S-T}} \text{ (eV)}$	-0.275	-0.403
$(\text{Ni} - \text{N})_{\text{S}} \text{ (Å)}$	4.206	2.963
$(\text{Ni} - \text{N})_{\text{T}} \text{ (Å)}$	2.056	2.122

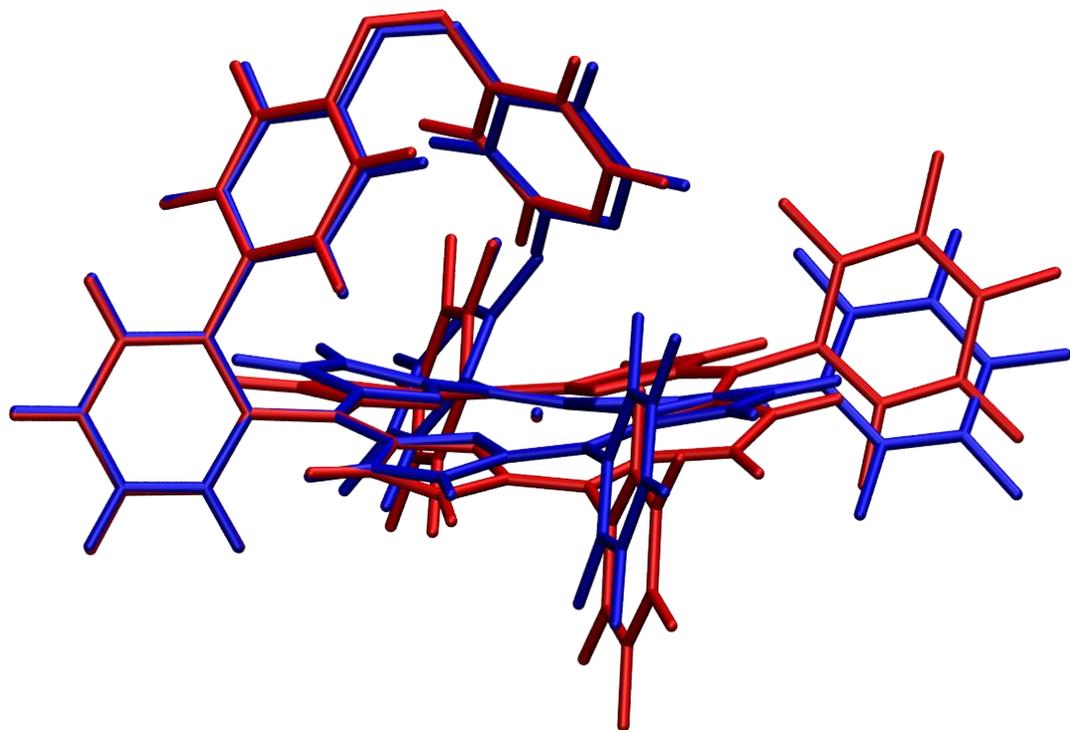
M11-L:

- Exchange: Dual-Range Exchange with LSDA and PBE functionals but with different mixing scheme for short- and long-range
- M11
- Hartree-Fock exchange (from 42.8% to 100% at long range)

Increase the HF exchange: - increases the adiabatic Gap and shorten the Ni - N bond distance



MN12-L vs. MN12-SX



Values	MN12-L	MN12-SX
$E_{\text{singlet}} \text{ (H)}$	-5495.28011221	-5495.77722521
$E_{\text{triplet}} \text{ (H)}$	-5495.25499857	-5495.76889684
$\text{Gap}_{\text{S-T}} \text{ (eV)}$	0.683	0.227
$(\text{Ni} - \text{N})_{\text{S}} \text{ (\AA)}$	3.288	3.321
$(\text{Ni} - \text{N})_{\text{T}} \text{ (\AA)}$	2.028	2.089

MN12-L:

- Exchange: LSDA with screening at long range

MN12-SX

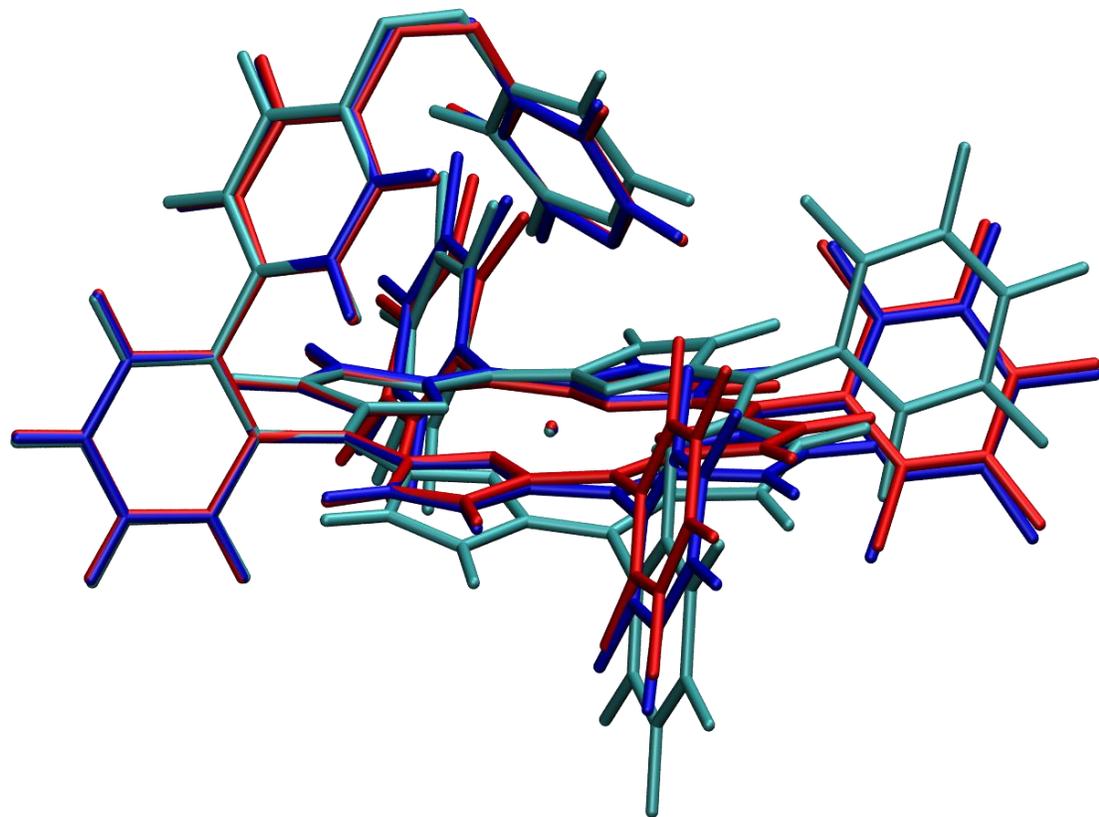
- Hartree-Fock exchange (from 25% to 36% at long range)

The lower energy is the singlet state energy !!!

Increase the HF exchange: - decreases the adiabatic Gap and a bit enlarge the Ni - N bond distance



Mo6-2x vs. M11 vs. MN12-SX



Values	M06-2X	M11	MN12-SX
E_{singlet} (H)	-5497.12149327	-5496.80021728	-5495.77722521
E_{triplet} (H)	-5497.15024947	-5496.81505495	-5495.76889684
$\text{Gap}_{\text{S-T}}$ (eV)	-0.782	-0.403	0.227
$(\text{Ni} - \text{N})_{\text{S}}$ (Å)	2.981	2.963	3.321
$(\text{Ni} - \text{N})_{\text{T}}$ (Å)	2.144	2.122	2.089

Lower energy:

M06-2X - triplet

M11 - triplet

MN12-SX - singlet

M06-2X to M11: - decreases the adiabatic Gap but give almost the same geometry

M11 to MN12-SX: - gives the singlet configuration as the lower energy and enlarge the Ni - N bond distance



Question: Which one?

Answer: I don't know.

What we know:

- Dispersion effects have a significant role - it needs to be included
- Excess amount of HF exchange can induce large errors in the static correlation effects
- Lack or small amount of HF exchange can induce large self-interaction errors

Solution: Use moderate HF exchange

Hopes that in this way you get **fortuitous cancellation of errors** between the static correlation effects and the self-interaction errors

Keep in mind:

- The “game” with HF exchange amount could never cover the “real” dispersion effects

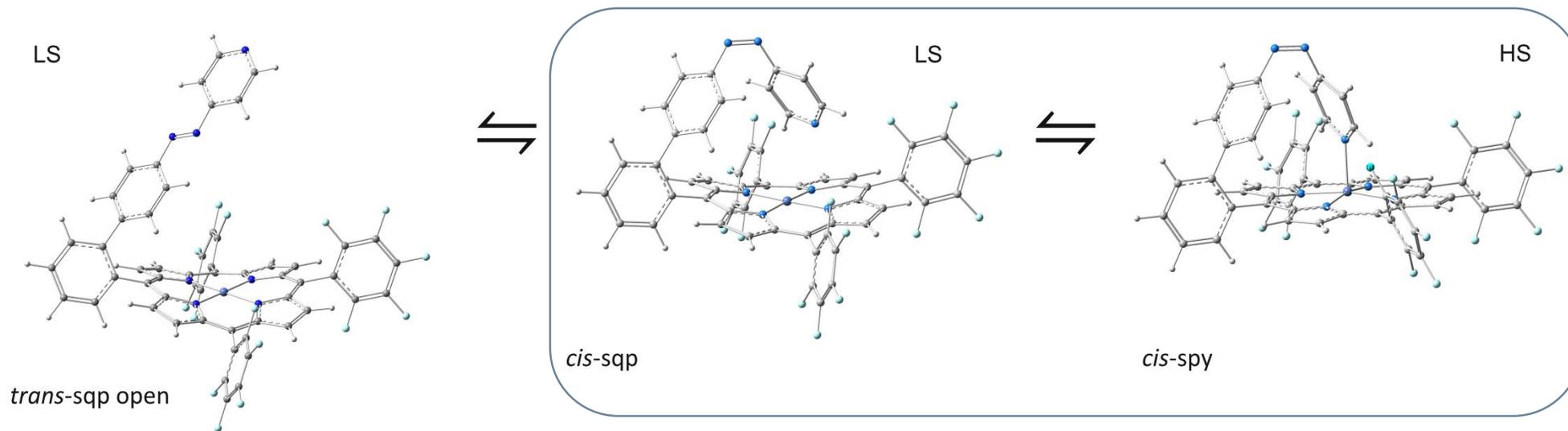


The best solution for our particular case:

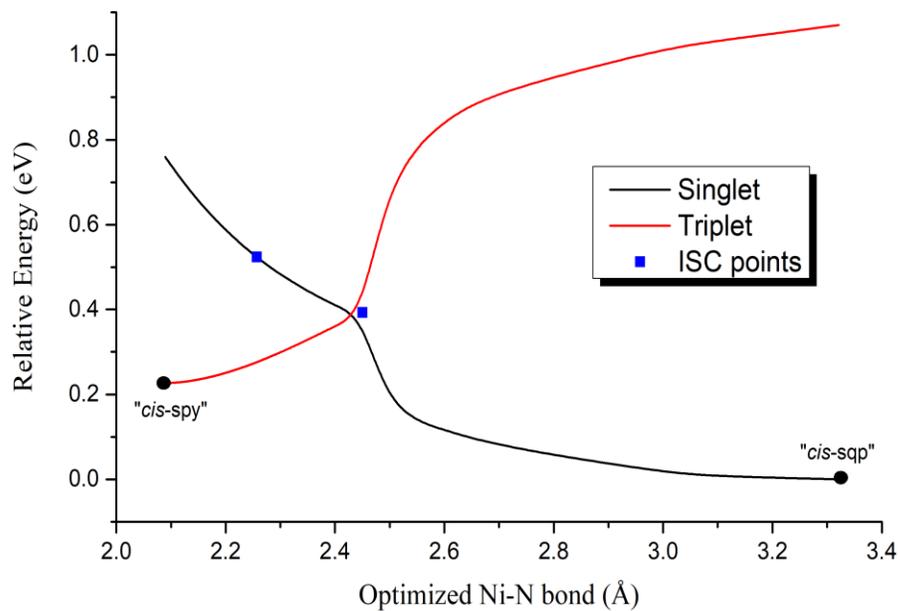
MN12-SX - also based on comparison with experimental data, like, UV absorption spectra



Results



Theory: MN12-SX/def2-TZVP

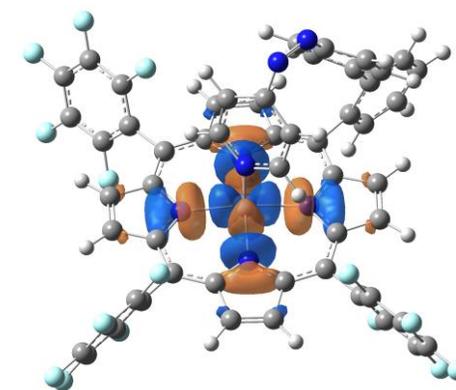
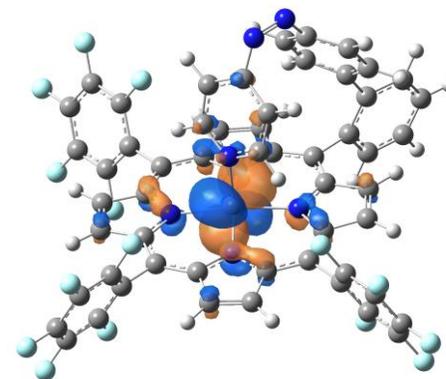
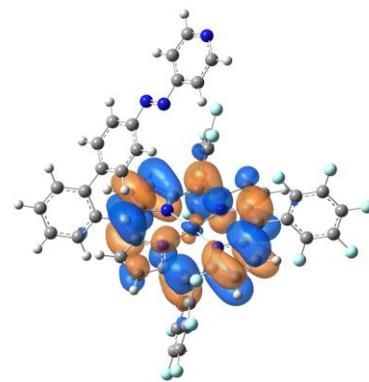
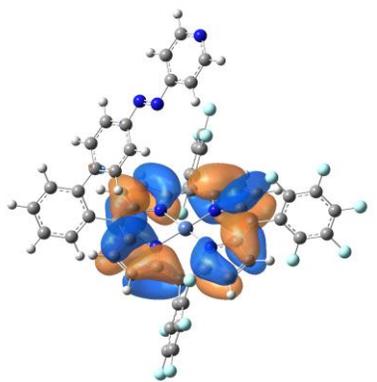
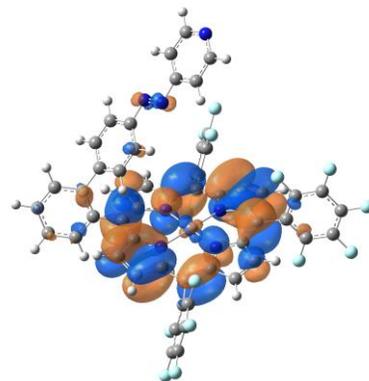
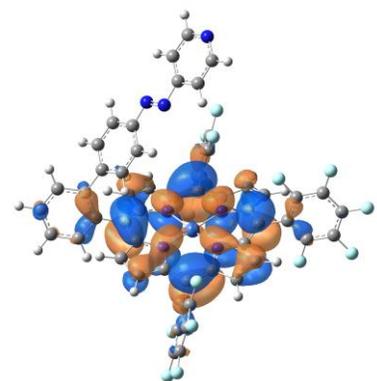


Geometry	$N_{\perp} \cdots Ni$ (Å)	Wiberg BO	$N_{\parallel} \cdots Ni$ (Å)	Wiberg BO	E^{Conf} (eV)
Singlet "cis-sqp"	3.321	0.010	1.934, 1.940 1.940, 1.941	0.500, 0.500 0.498, 0.494	0
Triplet "cis-spy"	2.089	0.272	2.031, 2.033 2.044, 2.044	0.331, 0.331 0.326, 0.325	0.235
ISC ₁	2.451	0.124	2.023, 2.026 2.034, 2.036	0.466, 0.466 0.462, 0.462	0.388
ISC ₂	2.259	0.174	1.982, 1.984 1.987, 1.987	0.489, 0.489 0.489, 0.488	0.524

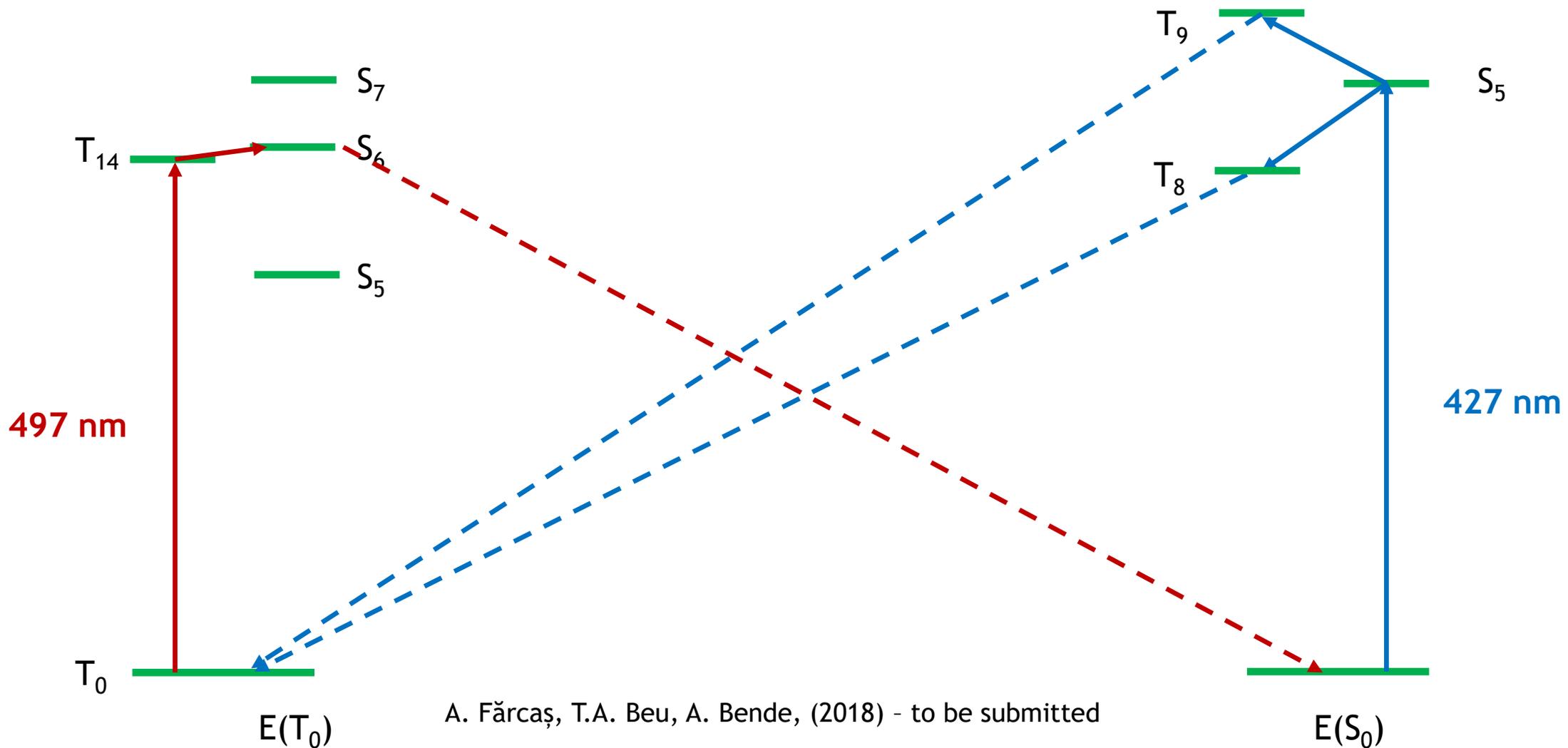
ISC - intersystem crossing



Excited State	Singlet		Excited State	Triplet	
	Nature	Value		Nature	Value
S_5	$\pi \rightarrow \pi$	497.23 (0.0029)	T_{14}	$M \rightarrow L$	427.41 (0.0011)
			T_{16}	$M \rightarrow L$	417.67 (0.0020)



Singlet-triplet transition over the excited states:



Financial support

- Program PN III - P4 - Cercetare Fundamentală și de Frontieră
- Project type : Proiecte de cercetare exploratorie (PCE2016)
- Project code: PN-III-P4-ID-PCE-2016-0208
- Contract Number: 64/2017
- Period: 2017-2019



Thank you for your attention

