Structural stability of Ni (II)-based macrocyclic-ligand complexes with square-pyramidal and octahedral coordination configuration

Attila Bende and Alex-Adrian Farcaș

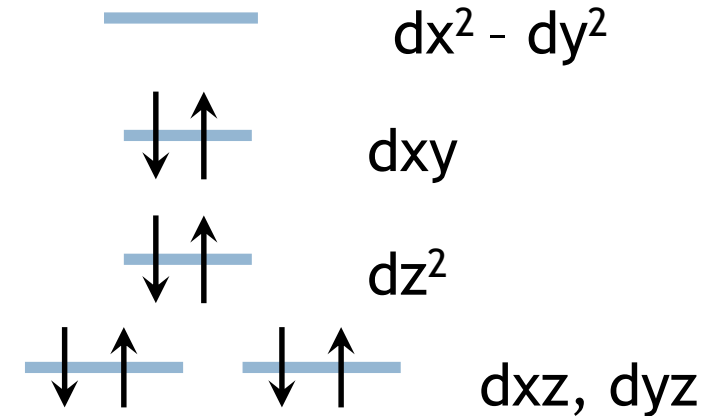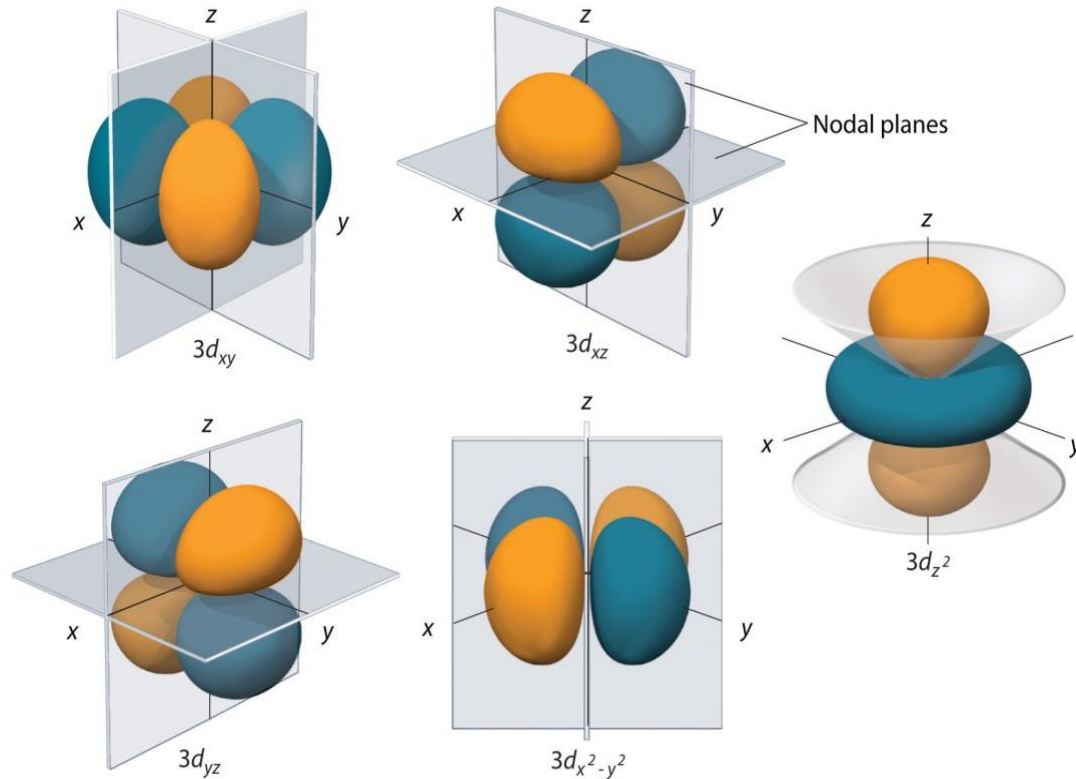INCDTIM Cluj-Napoca, Romania

Outline

- Spin transitions in organometallics

- Theoretical description using first principle methods

- Spin transitions in large molecular complexes

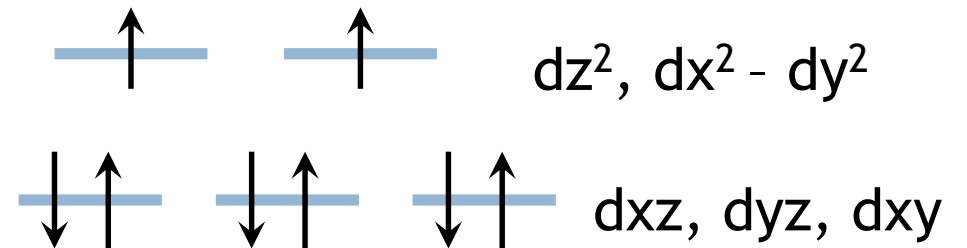- The role of different XC functionals

Spin transitions in organometallics

3d orbitals of Ni(II)

"Square-planar" coordination of the Ni(II) in **singlet** spin configuration

$dx^2 - dy^2$

dxy

dz^2

dxz, dyz

"Octahedral" coordination of the Ni(II) in **triplet** spin configuration

$dz^2, dx^2 - dy^2$

dxz, dyz, dxy

Spin transitions in organometallics

Organic ligand

Metal Centre

Charge transfer from the "electron reach" ligand to the positively charged metal centre
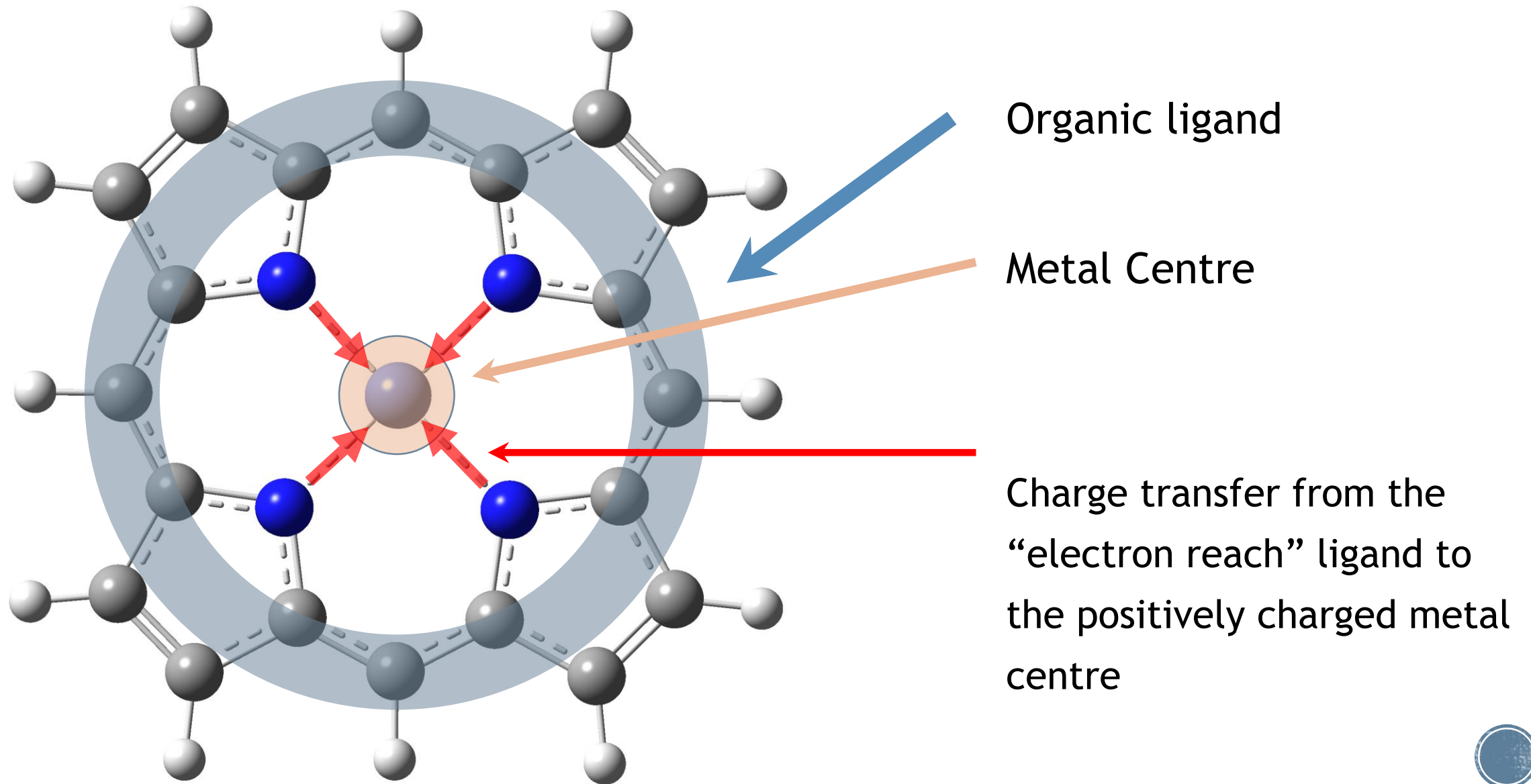
Theoretical description using first principle methods

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

⟹   Needs multireference methods MCSCF, MRCI, etc.

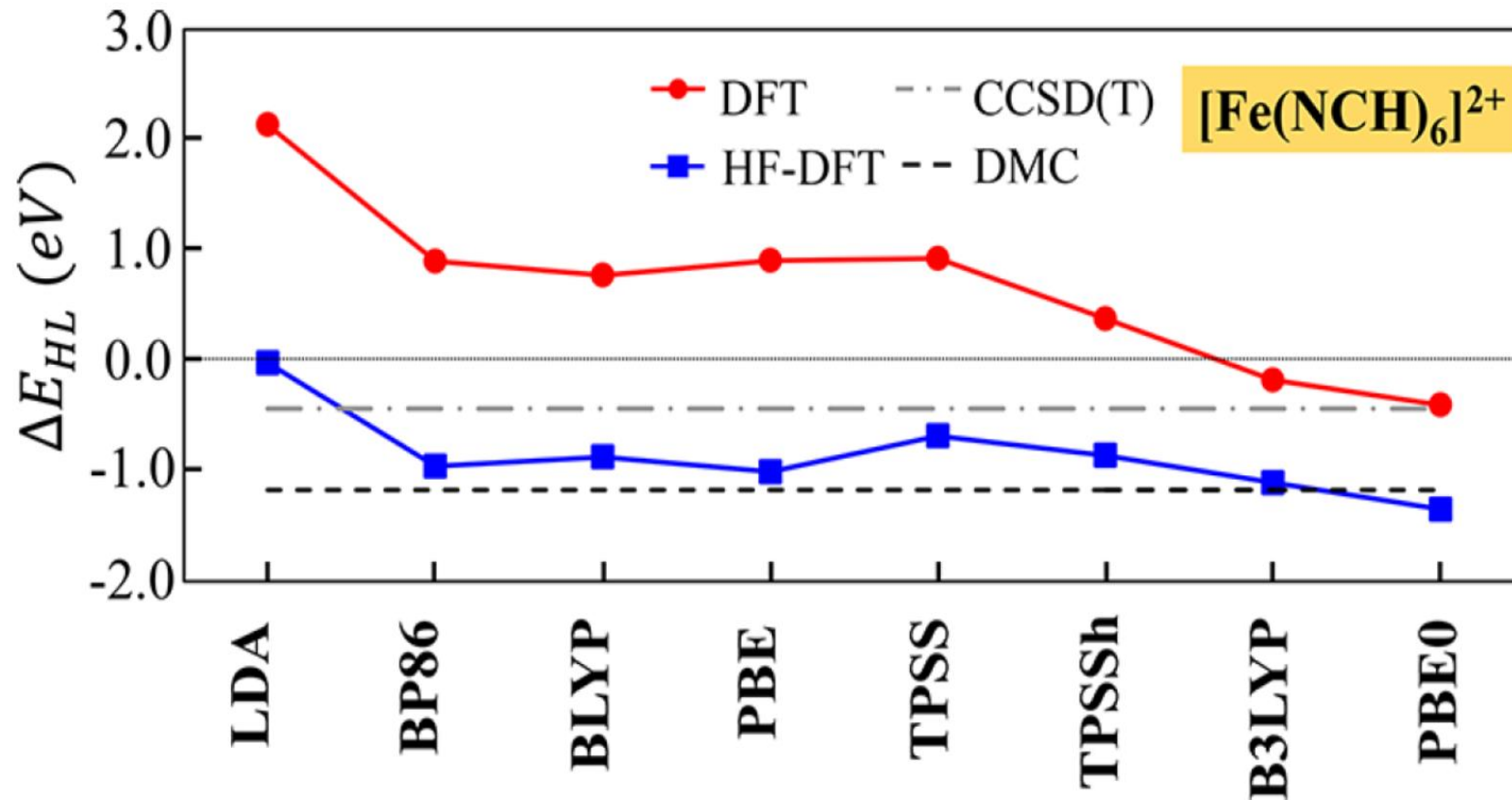Maximum: (20,10+5) – 20 electron with 10 occupied and 5 virtual orbitals

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)

Solution?
Try DFT

- **Dynamic electron correlation** due to the pair (or higher) correlation between the electrons.
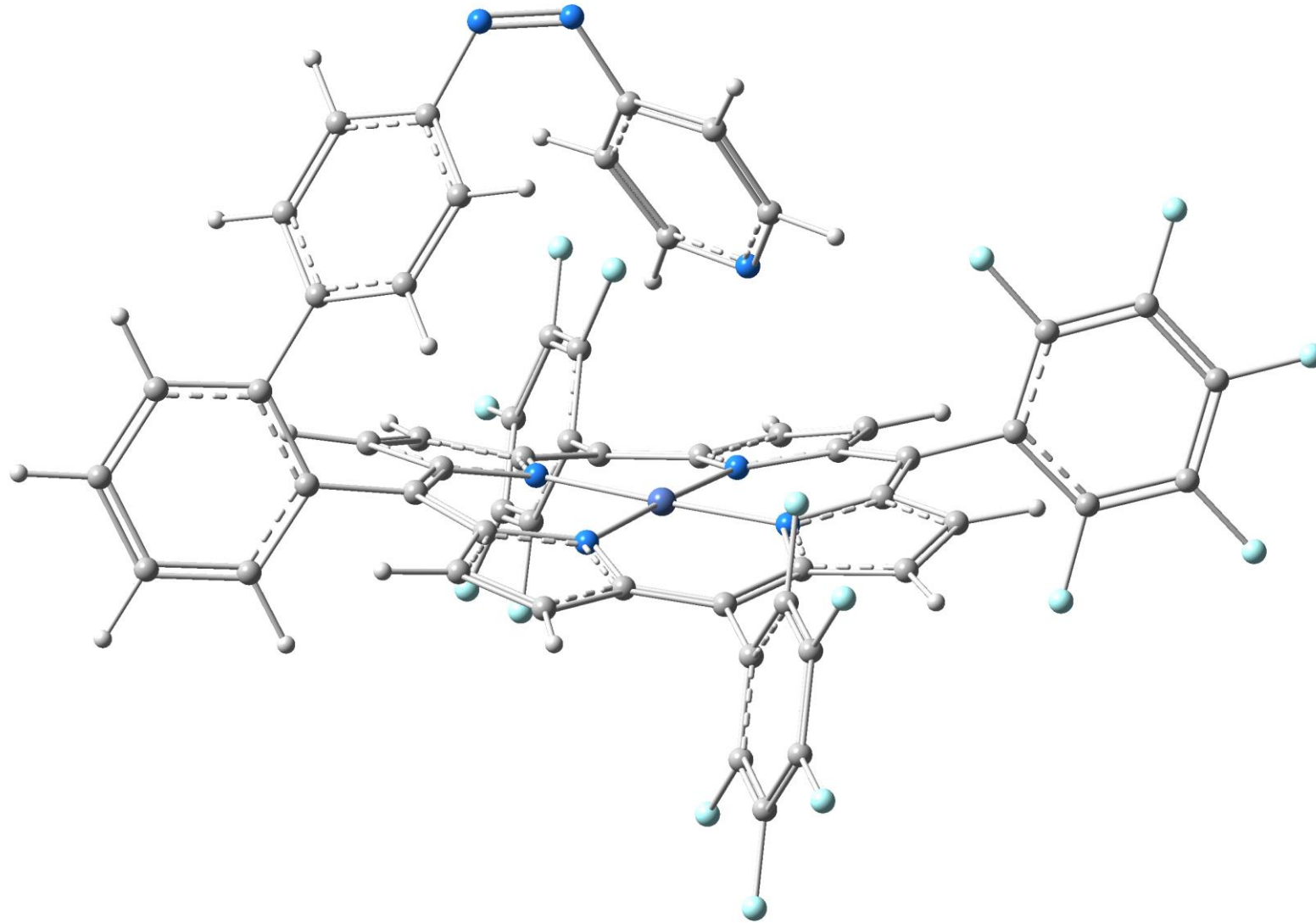
Question: Which one?

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)
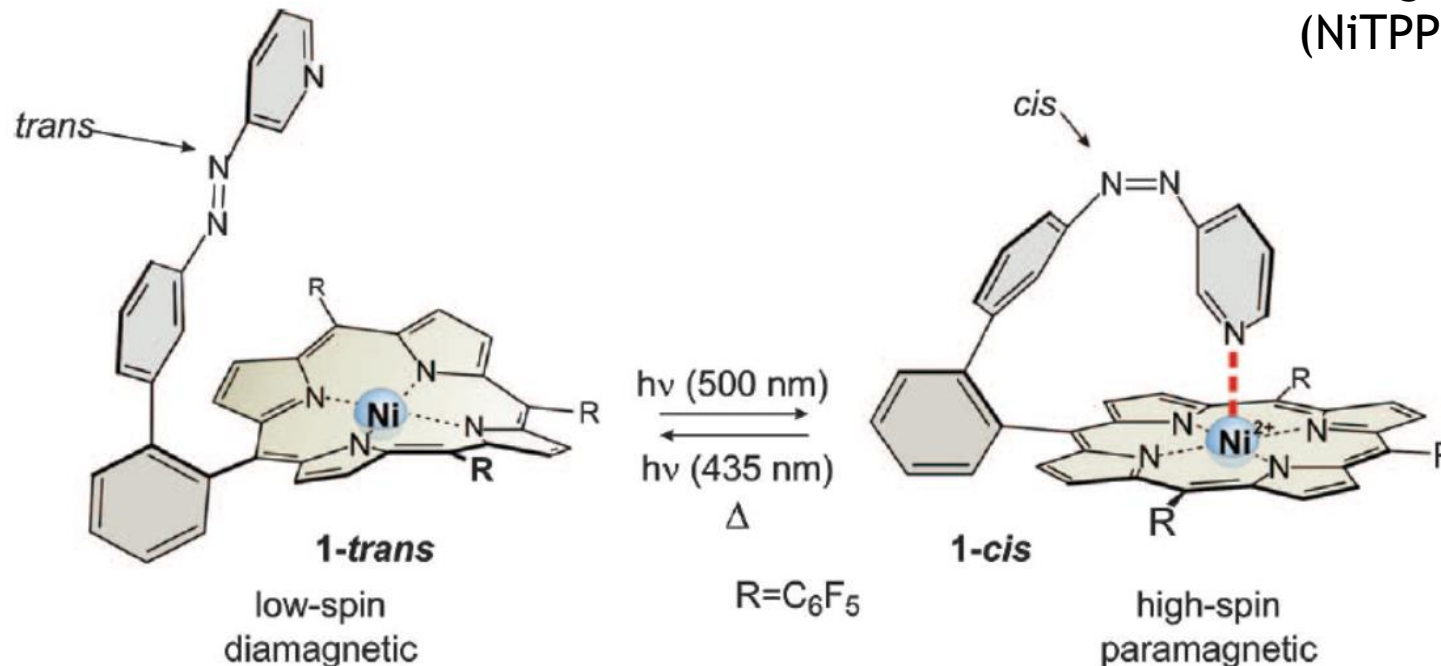
Spin transitions in large molecular complexes

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)
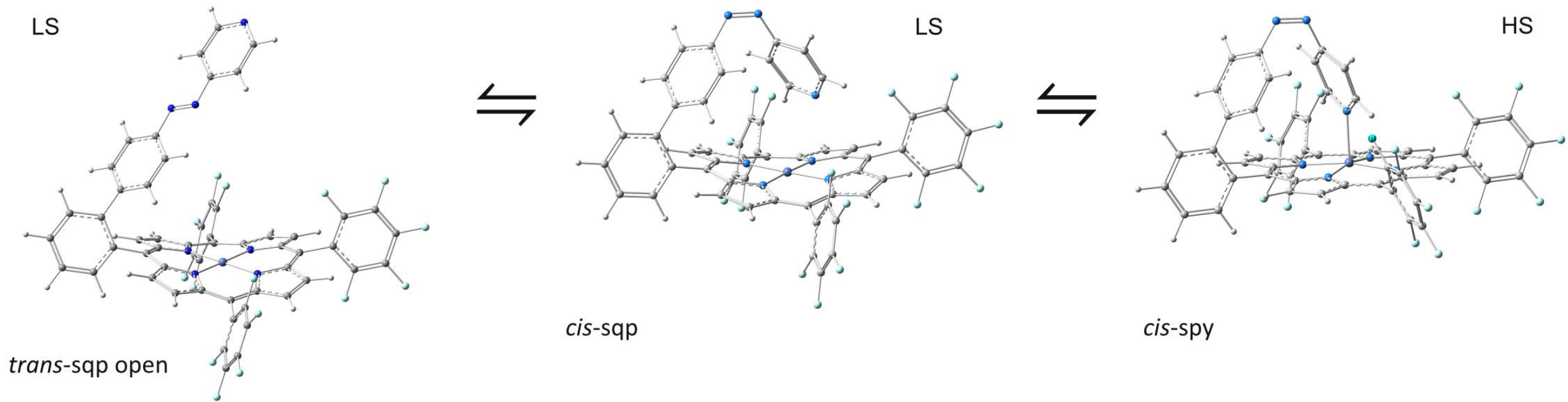

trans

cis

$h\nu$ (500 nm)

$h\nu$ (435 nm)

Δ

1-trans
low-spin
diamagnetic

$R = C_6F_5$

1-cis
high-spin
paramagnetic

LS

trans-sqp open

⇌

LS

cis-sqp

⇌

HS

cis-spy

Adiabatic energy gap: ΔE = E(LS) – E(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
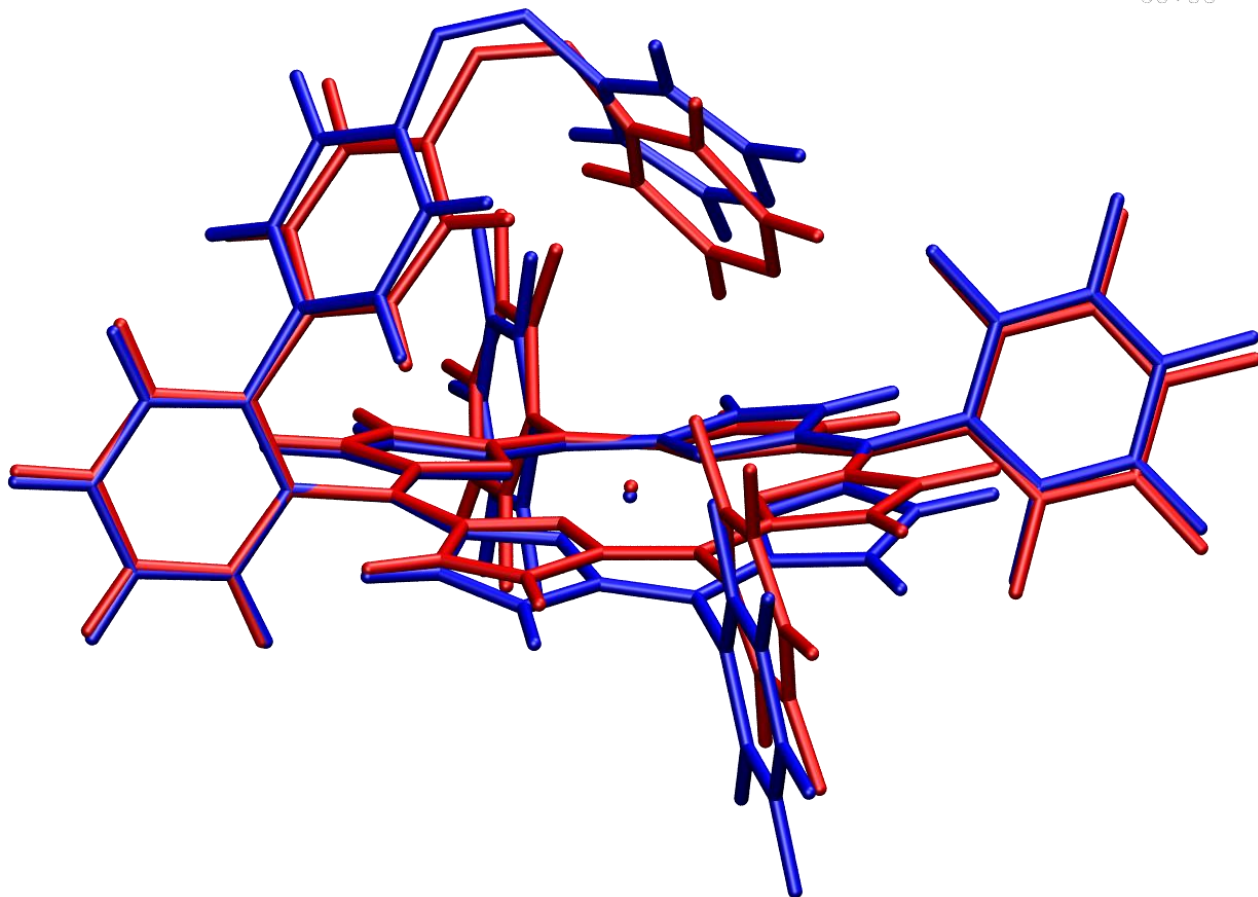
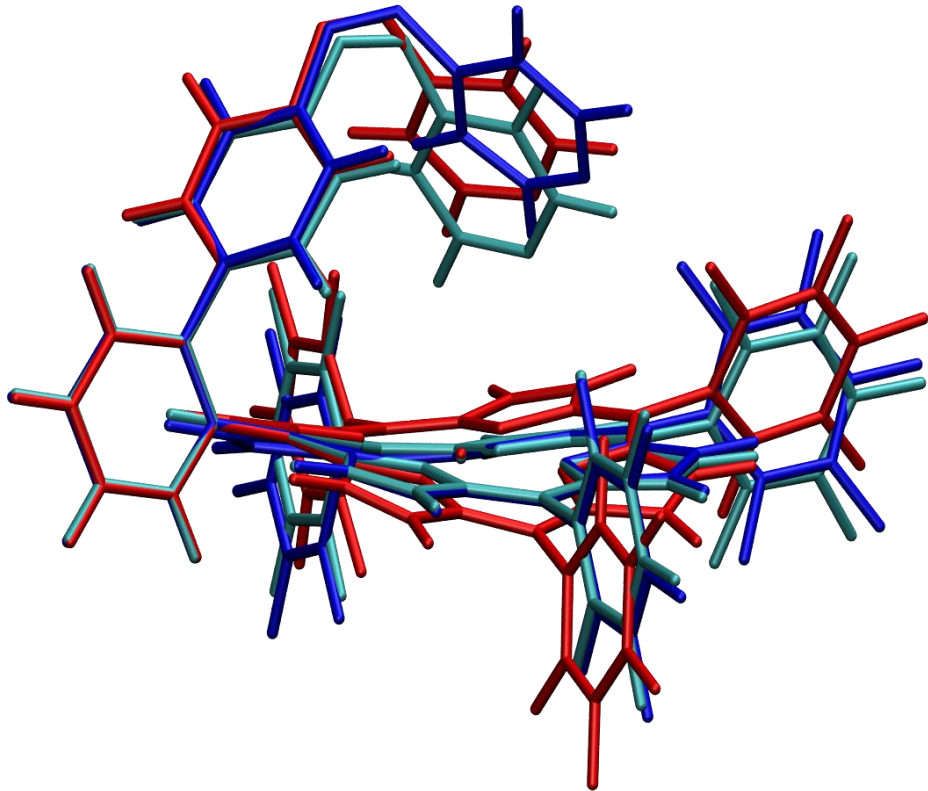| Values	B3LYP	B3LYP-D
$E_{singlet}$ (H)	-5498.61471573	-5498.92166059
$E_{triplet}$ (H)	-5498.61345808	-5498.92907580
Gap_{S-T} (eV)	0.034	-0.202
$(Ni - N)_S$ (Å)	4.982	3.918
$(Ni - N)_T$ (Å)	2.1220	2.093

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: ≈ **0.2 eV lower energy** and **1 Å shorter Ni - N bond distance**

B3LYP vs. CAM-B3LYP vs. CAM-B3LYP-D

| Values	B3LYP	CAM-B3LYP	CAM-B3LYP-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*
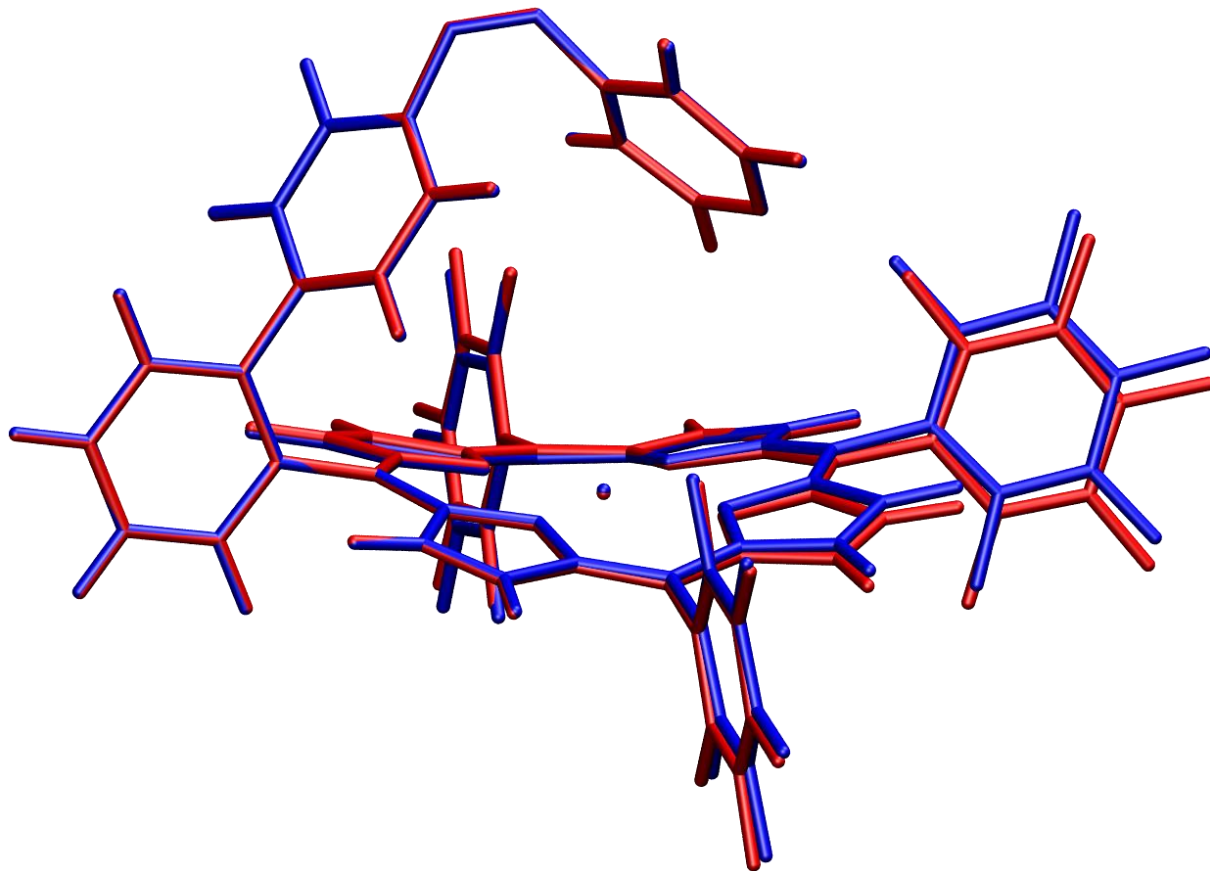
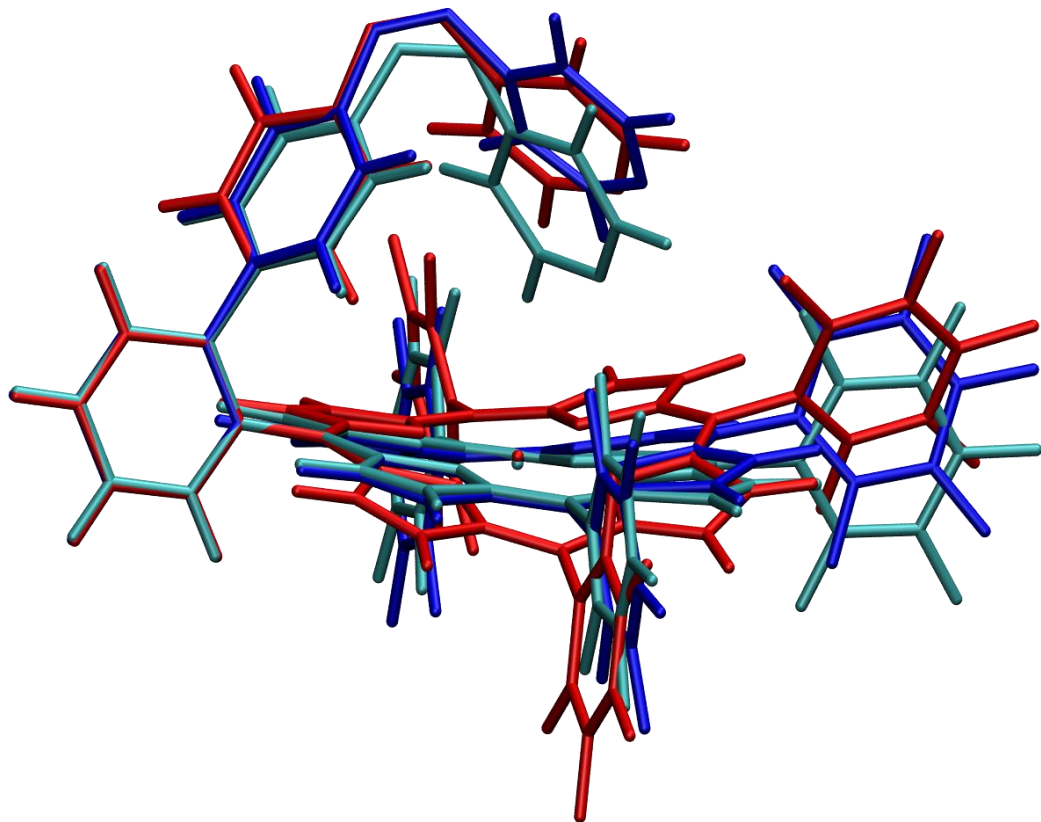| Values	B3LYP	B3LYP*
$E_{singlet}$ (H)	-5498.61471573	-5496.18990398
$E_{triplet}$ (H)	-5498.61345808	-5496.18318044
Gap_{S-T} (eV)	0.034	0.183
$(Ni - N)_S$ (Å)	4.982	4.932
$(Ni - N)_T$ (Å)	2.1220	2.093

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: ≈ **0.15 eV higher energy** but **NO Ni – N bond distance changes**

B3LYP vs. HSE06 vs. ωB97XD

| Values	B3LYP	HSE06	ωB97XD
$E_{singlet}$ (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

ωB97XD

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

M06-L vs. M06 vs. M06-2X
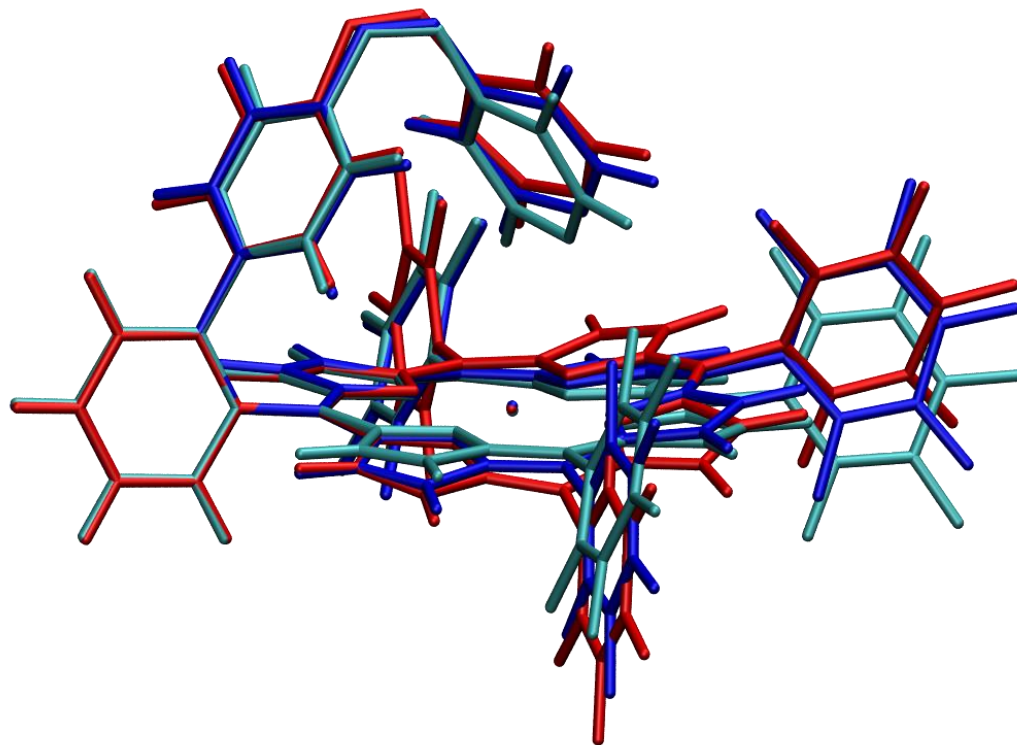
| Values	M06-L	M06 (27%)	M06-2X (54%)
$E_{singlet}$ (H)	-5498.03480956	-5496.26727825	-5497.12149327
$E_{triplet}$ (H)	-5498.04036581	-5496.26884836	-5497.15024947
Gap_{S-T} (eV)	-0.151	-0.043	-0.782
$(Ni-N)_S$ (Å)	3.415	3.723	2.981
$(Ni-N)_T$ (Å)	2.107	2.097	2.144

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
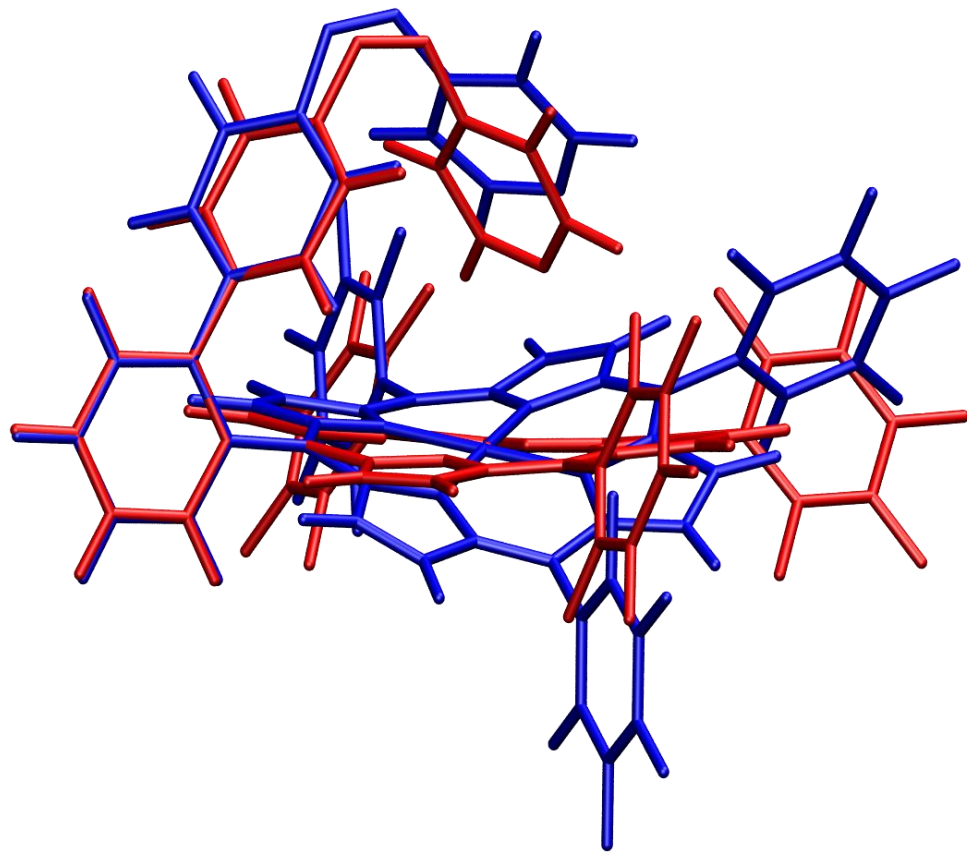
| Values	M11-L	M11
$E_{singlet}$ (H)	-5497.71462536	-5496.80021728
$E_{triplet}$ (H)	-5497.72473013	-5496.81505495
Gap_{S-T} (eV)	-0.275	-0.403
$(Ni-N)_S$ (Å)	4.206	2.963
$(Ni-N)_T$ (Å)	2.056	2.122

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
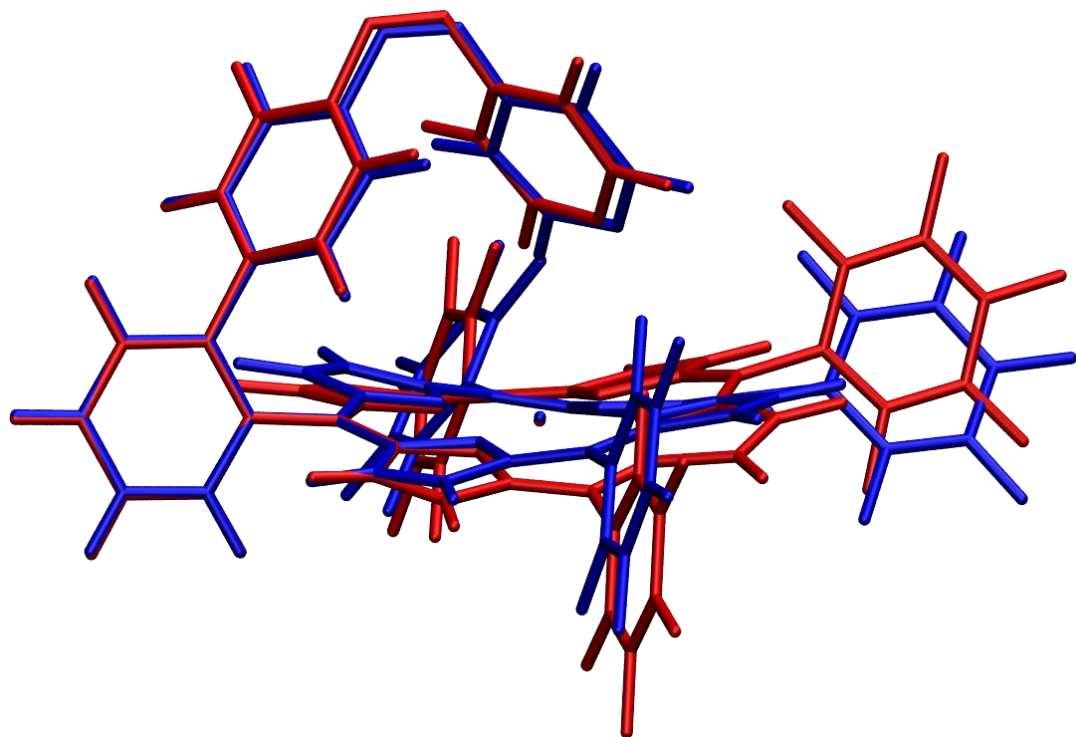
Values	MN12-L	MN12-SX
$E_{singlet}$ (H)	-5495.28011221	-5495.77722521
$E_{triplet}$ (H)	-5495.25499857	-5495.76889684
Gap_{S-T} (eV)	0.683	0.227
$(Ni - N)_S$ (Å)	3.288	3.321
$(Ni - N)_T$ (Å)	2.028	2.089

MN12-L:

- Exchange: LSDA with screening at long range
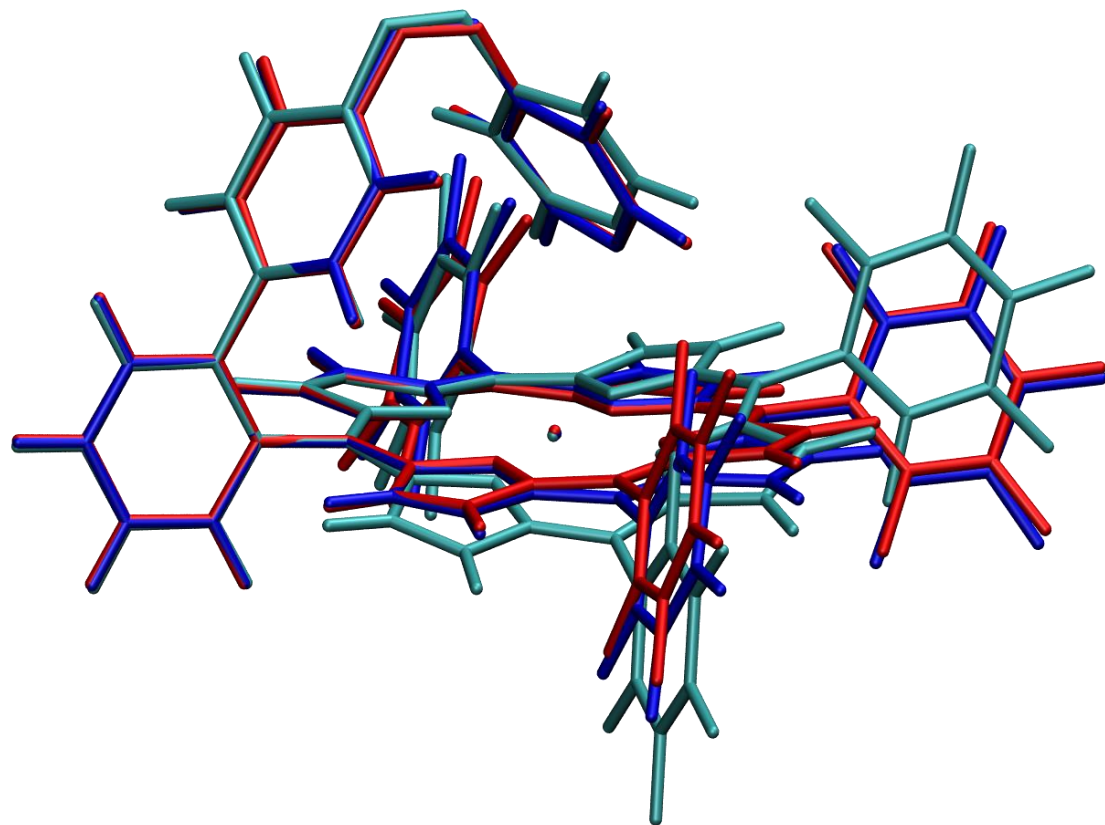
MN12-SX

- 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**

M06-2x 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
Gap_{S-T} (eV)	-0.782	-0.403	0.227
$(Ni-N)_S$ (Å)	2.981	2.963	3.321
$(Ni-N)_T$ (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

Financial support

- Program **PN III - P4** - Fundamental and Frontier Research

- Project code: PN-III-P4-ID-PCE-2016-0208

- Contract Number: 64/2017

- Period: 2017-2019

Thank you for your attention