

Light induced singlet-triplet transition in Ni(II)-based macrocyclic-ligand complexes Alex-Adrian Farcaș^{1,2}, Titus-Adrian Beu¹, Attila Bende²

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Abstract: Light induced singlet-triplet transition for Ni(II)-based macrocyclic-ligand complexes: Ni-tetrakis(pentafluorophenyl)porphyrin functionalized with a single phenazopyridine arm (NiTPP-PAPy) and Ni(II)-tetrakis-porphyrin functionalized with two phenazopyridine arms (NiTP-biPAPy) have been investigating using time-dependent density functional theory ^{1,2}. The calculations have been performed using the MN12-SX exchange correlation functional combined with the def2-TZVP basis set ^{3,4,5}. The singlet-triplet spin transitions have been characterized by searching for the intersystem crossing (ISC) point between the two potential energy surfaces of the ground state: singlet and triplet spin states. The strength of the spin-orbit coupling for the ISC geometry was also computed. The active electronic excited states involved in the light induced spin transitions were identified both for singlet and triplet excited electronic states. The presence of the moderate high barriers defined by the minimum energy crossing points between the singlet and triplet equilibrium



geometries of the NiTPP-PAPy and NiTP-biPAPy supramolecular complexes might be able to prevent the thermal-driven spin transition and thus facilitates the light-induced spin flip.





Fig. 2. The relative conformational energy values for singlet and triplet spin configurations of the NiTPP-PAPy molecular complex along the "minimal path" of the $N \perp \dots Ni$ atomic distance as well as the ISC points localized on the potential energy hyper-surface.

Fig. 1. The equilibrium geometries for the singlet "cis-sqp" and the triplet "cis-oct" spin configurations of the NiTP-biPAPy molecular complex.

Computational details: The equilibrium geometry structures of different Ni(II)macrocyclic ligand complexes with square-pyramidal and octahedral ligand-metal coordination with singlet and triplet spin states were calculated at the density functional theory (DFT) level using the MN12-SX exchange correlation (XC) functional⁶ together with the Def2-TZVP basis set. The charge distribution analysis was performed using the natural population analysis (NPA) method^{7,8} through the NBO module⁹ built in the GAUSSIAN 09 package. The molecular excited states were calculated using time-dependent density functional theory (TDDFT) . Localization of the intersystem crossing (ISC)¹⁰ points (more precisely the minimum energy crossing point (MECP)) between the singlet and triplet spin states on the potential energy surface was performed using a homemade routine based on the "Penalty function", algorithm proposed by Ciminelli et al¹ and choosing similar optimization parameters as it was proposed by Keal et al¹¹. The spin transition between lower and higher spin states depends not only on the energetically conditions defined by the crossing profile of the potential energy surfaces, but also from the magnitude of the spin orbit (SO) coupling.



Fig. 4. The trans-sqp open, cis-sqp and cis-spy geometries of the low-(LS) and high-spin (HS) electronic configuration of the Ni-tetrakis(pentafluorophenyl)porphyrin functionalized with a single phenazopyridine arm in square-pyramidal ligand metal coordination. For the simplicity, the Hydrogen atoms were removed and the pentafluorophenyl residues are marked with R.

Fig. 5. The theoretical UV absorption spectra calculated with and without spin orbit effects for the
singlet spin configuration of the cis-sqp equilibrium geometry at TD-DFT/TPSSh/def2-TZVP level o
theory.

Exc. State	Singlet		Exc. State	Triplet		Exc. State	Singlet		Exc. State	Triplet	
	Nature	Value		Nature	Value		Value	Nature		Value	Nature
S ₁	d—→d	529.45	T ₁	d—→d	1066.83	S_1	d→d	545.24	T ₁	d→d	833.67
	MC	(0.0000)		MC	(0.0000)		MC	(0.0000)		MC	(0.000)
S_2	$d \rightarrow d$	526.11	T_2	d→d	1039.20	S_2	$d \rightarrow d$	542.70	T_2	d→d	819.62
	MC	(0.0000)		MC	(0.0000)		MC	(0.0000)		MC	(0.0000)
S ₃	$d \rightarrow d$	525.90	T ₃	d—→d	672.19	S_3	$d \rightarrow d$	541.64	T_3	$n \longrightarrow \pi$	656.68
-	MC	(0.0001)	-	MC	(0.0000)		MC	(0.0000)		$n \longrightarrow M$	(0.0000)
S_4	$\pi \longrightarrow \pi$	506.33	T ₄	$n \longrightarrow \pi$	657.16				-	LC,LMCT	
	LC	(0.0112)		LC	(0.0004)	S_4	$\pi \longrightarrow \pi$	490.59	T_4	$n,\pi \longrightarrow \pi$	653.85
S ₅	$\pi \longrightarrow \pi$	503.95	T ₅	$n \longrightarrow \pi$	636.64		LC,LMCT	(0.0046)		$\pi \longrightarrow M$	(0.0003)
0	LC	(0.0021)	0	LC	(0.0002)	C		497.00	т	LC,LMCT	57415
S ₆	$n \longrightarrow \pi$	475.82	T ₆	$\pi \longrightarrow \pi$	599.59	3_5	$n \rightarrow \pi$	487.99	15	$\pi \longrightarrow \pi$	5/4.15
0	PAPv	(0.0345)	0	LC	(0.0003)	S.		(0.0012)	Т		(0.0001)
S_7	$\pi \longrightarrow \pi$	468.40	T_7	$\pi \longrightarrow \pi$	579.12	36		(0.0056)	16	$\pi \longrightarrow M$	(0,0001)
-7	LLCT	(0.0247)	-7	$\pi \longrightarrow M$	(0.0002)		HLC1	(0.0050)		LC LMCT	(0.0001)
		(010-17)		LLCT.LMCT	(010002)	S-	$\pi \longrightarrow \pi$	426.38	T_{7}	$M \rightarrow L$	562.72
Se	$\pi \longrightarrow \pi$	436.19	То	M→L	542.62	-,	LLCT	(0.0262)	- /		(0.0000)
	LLCT	(0.0008)	-8		(0.0000)	S ₈	$\pi \longrightarrow \pi$	421.12	T ₈	M→L	537.63
So	M—J.	414.55	То	M—→I.	529.98	0	LLCT	(0.0027)	0		(0.0000)
59		(0.0004)	-9		(0.0096)	S ₉	$n \longrightarrow \pi$	418.00	T9	$L \longrightarrow \pi$	527.38
Sto	$\pi \longrightarrow \pi$	388.99	Tio	$\pi \longrightarrow \pi$	521.88	-	LLCT	(0.0054)			(0.0002)
510		(0.1212)	110	$n \longrightarrow \pi$	(0.0010)	S ₁₀	$M \longrightarrow L$	414.68	T ₁₀	$L {\longrightarrow} \pi$	525.06
	LLCT	(0.1212)			(0.0010)			(0.0000)			(0.0004)
			Τ	M_J	433 60				T_{15}	$n \longrightarrow \pi$	463.30
			14	M—>L	(0.0012)					LLCT	(0.0011)
			т	мл	(0.0013)				T ₁₉	$\pi \longrightarrow \pi$	427.46
			I ₁₅	IMI→T	424.23					LLCT	(0.0028)

Conclusions:

In the case of square-pyramidal coordination configuration of the NiTPP-PAPy supramolecular complex, two intersystem crossing points were identified. Using the "Penalty function", the same ISC point was located as the one obtained through the intersection of the energy minimum pathways of the N \perp ...Ni ligand bond considered with singlet and triplet spin configuration. The experimental vertical excitation energies obtained both for singlet and triplet spin configurations were reproduced with a good accuracy by the theoretical calculations. In the case of NiTP-biPAPy complex with octahedral coordination, the ISC geometry with asymmetric phenazopyridine arms configuration gives lower energy barrier than the "symmetric" case and thus it is more likely to be involved in the spin transition between the ground states with singlet and triplet spin configurations.

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Table 1. The first ten vertical excitation energies (in nm) and oscillator strengths (in parenthesis), as well as the nature of the transitions for singlet ("trans-sqp") and triplet ("cis-spy") spin configurations of NiTPP-PAPy molecular complex. (L=ligand, M=metal, MC=metal centered, LC=ligand centered, LLCT=ligand-toligand charge transfer, LMCT=ligand-to-metal charge transfer).

Table 2. The first ten vertical excitation energies (in nm) and oscillator strengths (in parenthesis), as well as the nature of the transitions for singlet and triplet spin configurations of NiTP-biPAPy molecular complex. (L=ligand, M=metal, MC=metal centered, LC=ligand centered, LLCT=ligand-to-ligand charge transfer, LMCT=ligand-to-metal charge transfer).

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