



Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

ESI for

On the Structures, Spin States, and Optical Properties of Titanium, Platinum, and Iron Azacalixphyrins: A DFT Study[†]

Gabriel Marchand,^{*a} Olivier Siri^b and Denis Jacquemin^{*a,c}

^a CEISAM, UMR CNRS 6230, BP 92208, Université de Nantes, 2, Rue de la Houssinière, 44322 Nantes, Cedex 3, France. E-mail: Gabriel.Marchand@univ-nantes.fr

^b Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), UMR CNRS 7325, Aix-Marseille Université, Campus de Luminy, case 913, F-13288 Marseille Cedex 09, France.

^c Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 5, France. E-mail: Denis.Jacquemin@univ-nantes.fr

S1 Influence of the selected atomic basis set

	Atomic Basis Set	$S = 0$	$S = 1$	$S = 2$
Fe- 2^{2+}	6-31G(d) + LANL2DZ	19.1	0.0	15.2
	6-31G(d)	18.3	0.0	13.5
	6-311++G(d,p)	17.1	0.0	13.9

Table S1 Relative free energies, ΔG (in kcal.mol $^{-1}$), of the low ($S=0$), intermediate ($S=1$), and high ($S=2$) spin states of Fe- 2^{2+} obtained with the OLYP functional and the 6-31G(d) + LANL2DZ, 6-31G(d), and 6-311++G(d,p) atomic basis sets. The most stable state is selected as reference.

	Atomic Basis Set	$S = 0$		$S = 1$		$S = 2$	
		$R_{\text{Fe}-\text{N}}$	$R_{\text{Fe}-\text{C}}$	$R_{\text{Fe}-\text{N}}$	$R_{\text{Fe}-\text{C}}$	$R_{\text{Fe}-\text{N}}$	$R_{\text{Fe}-\text{C}}$
Fe- 2^{2+}	6-31G(d) + LANL2DZ	1.964	1.904	2.008	1.956	2.019	1.978
	6-31G(d)	1.946	1.926	1.972	1.941	1.964	1.967
	6-311++G(d,p)	1.982	1.974	1.992	1.956	1.982	1.980

Table S2 Fe-N and Fe-C bond lengths, $R_{\text{Fe}-\text{N}}$ and $R_{\text{Fe}-\text{C}}$ (in Å), of the low, intermediate, and high spin states of Fe- 2^{2+} obtained with the OLYP functional and the 6-31G(d) + LANL2DZ, 6-31G(d), and 6-311++G(d,p) atomic basis sets.

S2 Solvation effects on the spin state energetics and absorption spectra

S2.1 Spin state energetics

ACP Complex	Media	$S = 0$	$S = 1$	$S = 2$
Ti- 1 ²⁺	Gas Phase	0.0 (S_4)	17.1 (S_4)	42.3 (S_4)
	DMSO	0.0 (S_4)	20.7 (S_4)	45.1 (S_4)
Ti- 1(NH₃)₂²⁺	Gas Phase	0.0 (S_4)	9.9 (S_4)	29.9 (S_4)
	DMSO	0.0 (S_4)	11.6 (S_4)	29.7 (S_4)
Ti- 1(Br)₂	Gas Phase	0.0 (S_4)	5.1 (S_4)	28.2 (S_4)
	DMSO	0.0 (S_4)	6.4 (S_4)	28.9 (S_4)
Pt- 1(NH₃)₂²⁺	Gas Phase	0.0 (S_4)	25.6 (S_4)	52.5 (S_4)
	DMSO	0.0 (S_4)	24.5 (S_4)	52.8 (S_4)
Pt- 1(Br)₂	Gas Phase	0.0 (D_{2d})	12.4 (S_4)	39.0 (S_4)
	DMSO	0.0 (D_{2d})	13.8 (S_4)	44.3 (S_4)
Pt- 2 ²⁺	Gas Phase	0.0 (D_{2d})	23.9 (D_{2d})	57.0 (D_{2d})
	DMSO	0.0 (D_{2d})	23.5 (D_{2d})	57.8 (D_{2d})
Fe- 2 ²⁺	Gas Phase	30.1 (D_{2d})	0.0 (D_{2d})	17.9 (D_{2d})
	DMSO	30.9 (D_{2d})	0.0 (D_{2d})	14.3 (D_{2d})

Table S3 Relative free energies, ΔG (in kcal.mol⁻¹), of the low, intermediate, and high spin states of selected ACP metallic complexes in gas phase and in DMSO. In parentheses: the point group of the considered conformation, see main text. All values are obtained with the OLYP/6-31G(d)+LANL2DZ method and the PCM.

S2.2 Absorption spectra

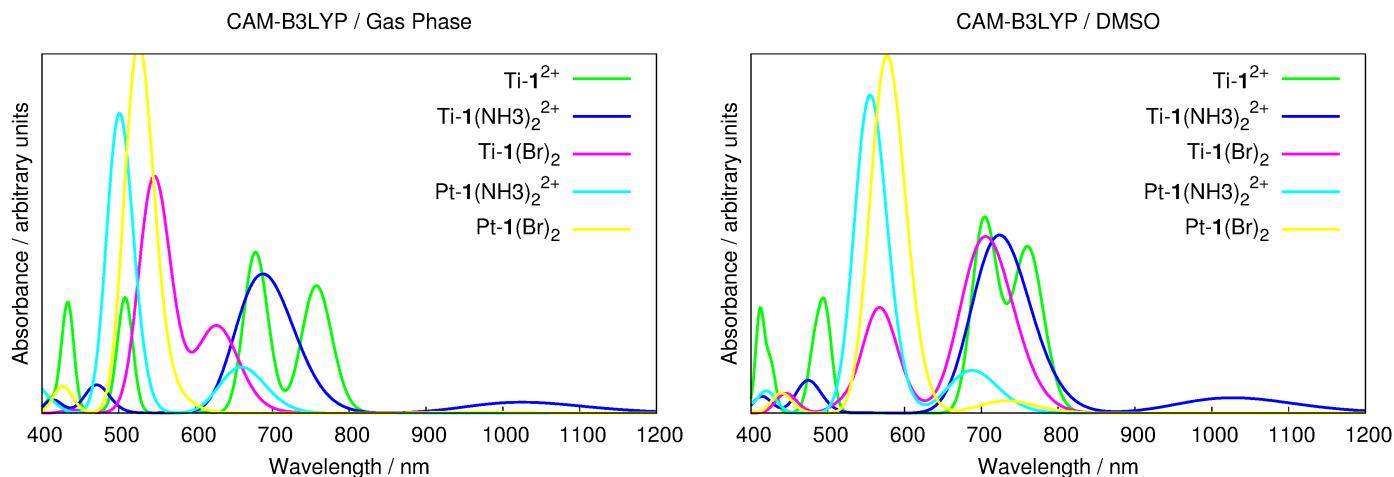


Fig. S1 Absorption spectra of the ACP precursor complexes, in gas phase and in DMSO.

S3 Influence of the DFT functional on the absorption spectra

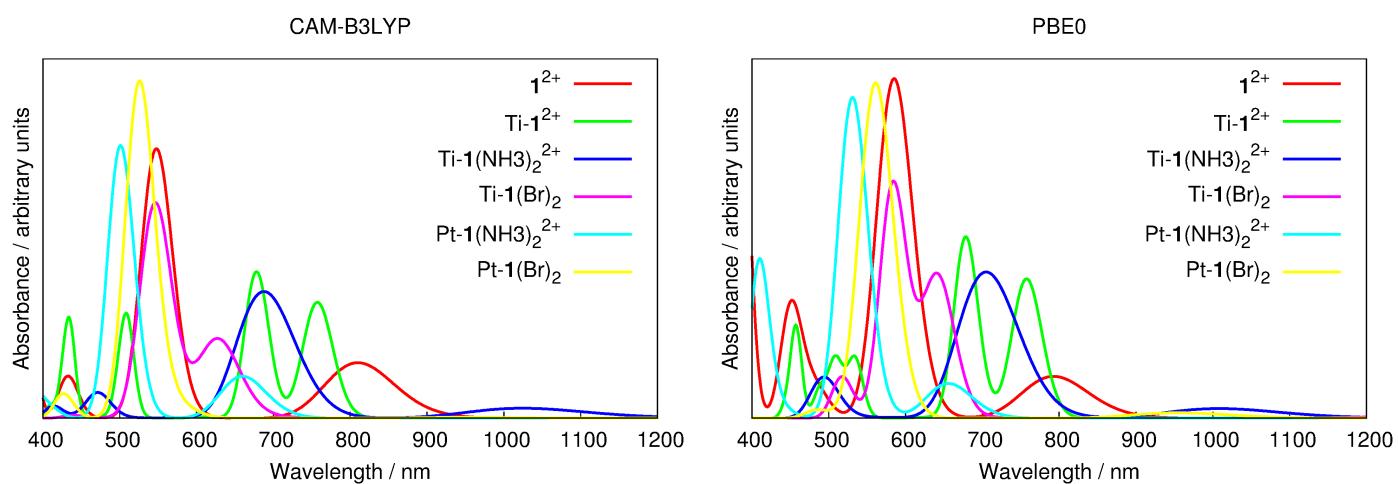


Fig. S2 Absorption spectra of the ACP complexes, obtained with the CAM-B3LYP and PBE0 functionals, in gas phase.

S4 Comparison between dicationic and neutral forms

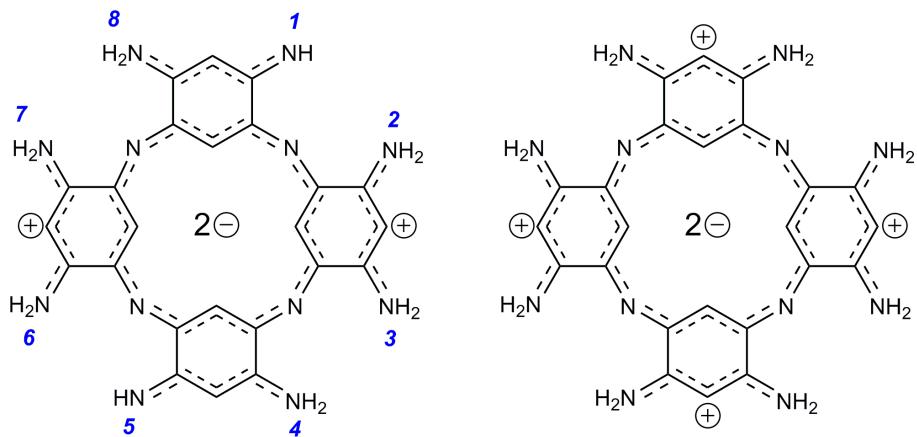


Fig. S3 Representation of the unsubstituted ACP, in its neutral (left) and diprotonated dicationic (right) forms. For the neutral form, the two imines are at positions 1 and 5, hence this is the '1-5' tautomer. The other tautomers, have different relative positions of the two imine groups.

		Tautomer										2H^+
	Symmetry	1-2	1-3	1-4	1-5	1-6	1-7	1-8	2-3	2-6	2-7	
Pt- 2^{2+}	$S = 0$	C_1	C_1	C_s	C_2	C_1	C_1	C_s	C_s	C_2	C_s	C_{2v}
	$S = 1$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	$S = 2$	22.6	21.6	28.1	27.6	20.4	21.1	-1.50	0.0	19.9	20.1	23.9
		50.6	50.7	56.8	57.7	52.8	53.8	25.0	26.2	57.8	58.1	57.0

Table S4 Spin-state energetics (ΔG values in $\text{kcal}\cdot\text{mol}^{-1}$) of Pt- 2^{2+} in its neutral (several tautomers) and diprotonated dicationic ("2H⁺") forms. All values obtained with the OLYP/6-31G(d)+LANL2DZ method. The most stable state is selected as reference for each conformer.

S5 Transition state geometry between the D_{2d} and S_4 conformations

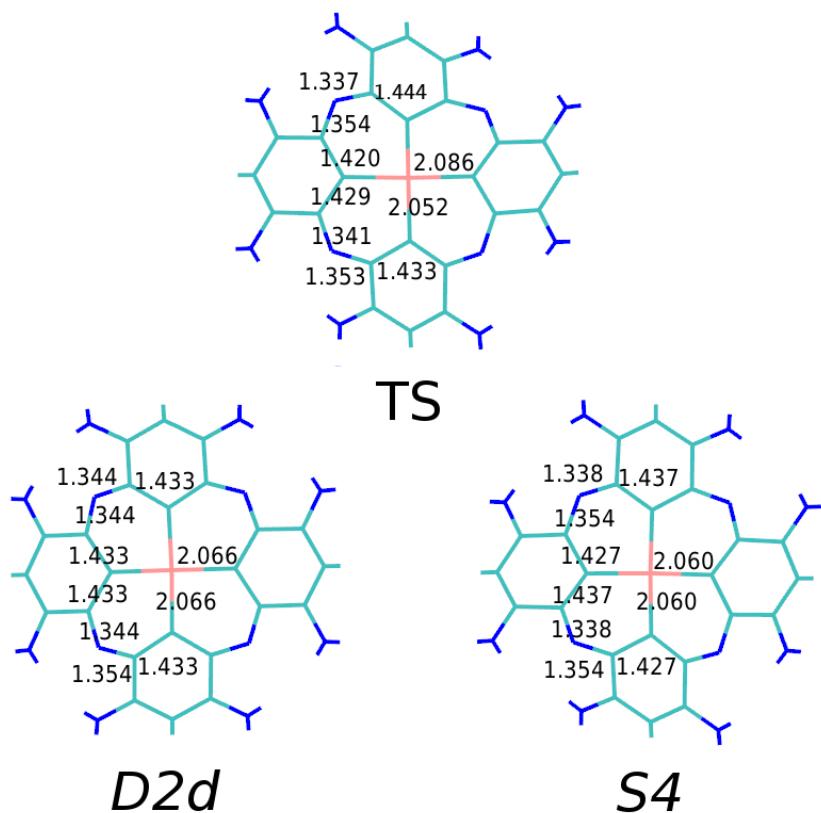


Fig. S4 Bond lengths measured for the D_{2d} and S_4 conformations, and in the intermediate (TS) structure between these two for the Ti-1²⁺ derivative.

S6 HOMO-HOMO-1 energy difference as a function of the degree of Jahn-Teller distortion

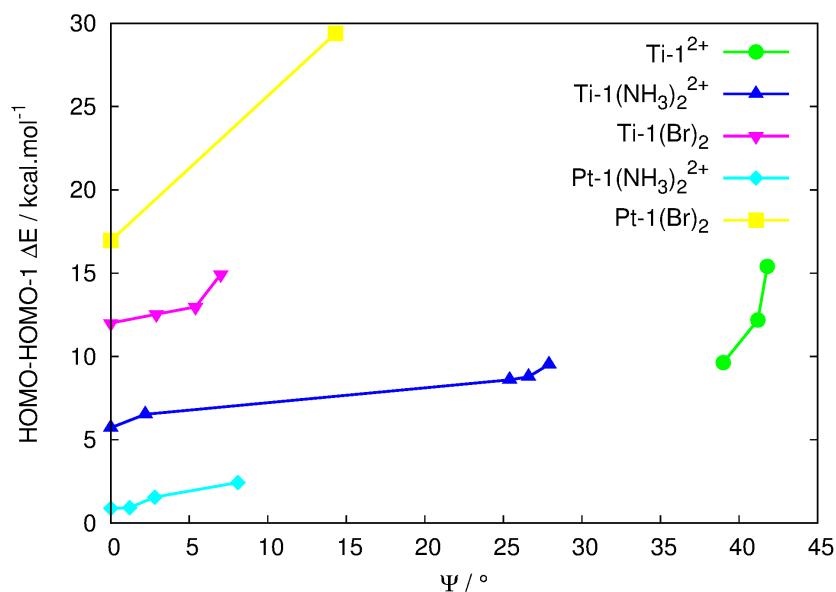


Fig. S5 HOMO-HOMO-1 energy difference (in $\text{kcal} \cdot \text{mol}^{-1}$) *versus* the amount of pseudo Jahn-Teller distortion ψ (in degrees) for different ACP complexes. The data have been collected using the DFT functional OLYP, M06-L, and PBE0.

S7 Transition energies and oscillator strengths obtained by TD-DFT

	1²⁺ <i>D_{2d}</i>	Ti-1²⁺ <i>S₄</i>	Ti-1(NH₃)₂²⁺ <i>S₄</i>	Ti-1(Br)₂ <i>S₄</i>	Pt-1(NH₃)₂²⁺ <i>D_{2d}</i>	Pt-1(Br)₂ <i>D_{2d}</i>	Pt-2²⁺ <i>D_{2d}</i>	Fe-2²⁺ <i>D_{2d}</i>
<i>S₁ ← S₀</i>	1.53 (0.06)	1.64 (0.13)	1.17 (0.01)	0.88 (0.00)	1.88 (0.05)	1.30 (0.00)	1.97 (0.23)	0.73 (0.00)
<i>S₂ ← S₀</i>	1.53 (0.06)	1.83 (0.17)	1.23 (0.01)	0.91 (0.00)	1.88 (0.05)	1.30 (0.00)	2.01 (0.05)	1.05 (0.00)
<i>S₃ ← S₀</i>	2.26 (0.31)	2.05 (0.00)	1.75 (0.14)	1.74 (0.00)	2.47 (0.31)	1.88 (0.00)	2.26 (0.00)	1.12 (0.00)
<i>S₄ ← S₀</i>	2.26 (0.31)	2.43 (0.10)	1.84 (0.19)	1.94 (0.00)	2.47 (0.31)	2.16 (0.03)	2.52 (0.21)	1.25 (0.00)
<i>S₅ ← S₀</i>	2.69 (0.00)	2.48 (0.04)	2.18 (0.00)	1.95 (0.00)	2.81 (0.00)	2.36 (0.38)	2.84 (0.00)	1.30 (0.00)
<i>S₆ ← S₀</i>	2.87 (0.10)	2.51 (0.00)	2.34 (0.00)	1.97 (0.09)	2.94 (0.00)	2.36 (0.38)	2.99 (0.07)	1.43 (0.00)
<i>S₇ ← S₀</i>	2.89 (0.00)	2.60 (0.00)	2.48 (0.00)	1.98 (0.09)	3.00 (0.02)	2.68 (0.00)	3.04 (0.00)	1.75 (0.00)
<i>S₈ ← S₀</i>	3.30 (0.32)	2.73 (0.00)	2.50 (0.00)	2.01 (0.00)	3.17 (0.05)	2.84 (0.00)	3.06 (0.21)	1.80 (0.00)
<i>S₉ ← S₀</i>	3.30 (0.32)	2.79 (0.01)	2.61 (0.03)	2.04 (0.00)	3.32 (0.00)	2.86 (0.00)	3.30 (0.04)	1.87 (0.01)
<i>S₁₀ ← S₀</i>	3.30 (0.00)	2.83 (0.00)	2.65 (0.01)	2.26 (0.23)	3.39 (0.00)	2.89 (0.00)	3.33 (0.00)	1.92 (0.00)

Table S5 First ten lowest-lying (singlet) vertical excitation energies (in eV) and corresponding oscillator strengths (in parentheses), for the titanium, platinum, and iron ACP complexes. All values have been obtained with the CAM-B3LYP functional.

S8 Frontier molecular orbitals of Pt-1-(NH₃)₂²⁺ and Pt-1(Br)₂

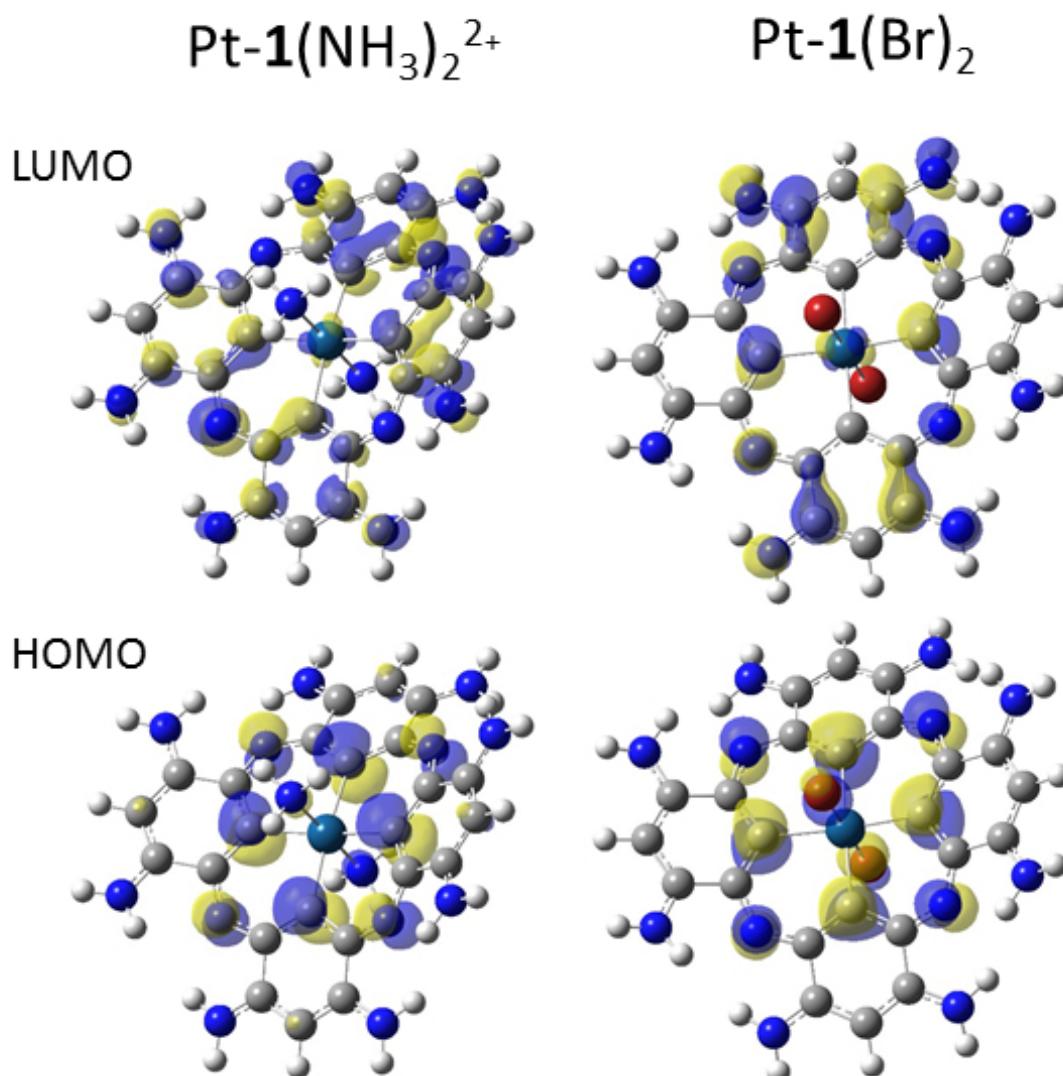


Fig. S6 HOMO and LUMO of Pt-1(NH₃)₂²⁺ and Pt-1(Br)₂.

S9 Molecular orbital energy diagram of Fe-2²⁺

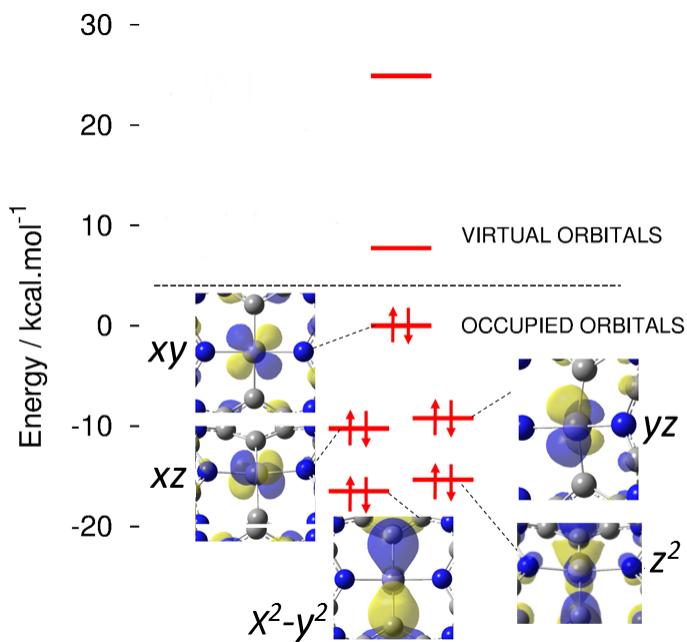


Fig. S7 Frontier molecular d -orbitals of Fe-2^{2+} and their energy splitting.