Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for 'Co(III) protoporphyrin IX chloride in solution: Spin-state and metal coordination revealed from resonant inelastic X-ray scattering and electronic structure calculations'

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	CoPP9-Cl S=2	CoPP9-Cl S=1	CoPP9-Cl S=0
Co-Cl bond distance (Å)	2.225	2.303	2.201
Co-N bond distance (Å)	2.101, 2.087, 2.093, 2.082	2.003, 2.008, 1.994, 2.003	1.994, 1.995, 1.989, 1.992
Cl-Co-N bond angle (°)	104.9, 102.3, 106.7, 104.7	93.6, 99.3, 95.4, 101.2	93.8, 95.2, 95.8, 96.7
N-Co-N bond angle (°)	86.4, 86.4, 86.1, 86.5	89.3, 89.2, 89.1, 89.2	89.6, 89.5, 89.3, 89.6
Total dipole moment (Debye)	1.14	3.69	1.38
Total single point energy (eV)	-100065.96	-100066.18	-100066.12

Table SI-1. The coordination of cobalt in CoPPIX chloride varying with different spin configurations according to the B3LYP/def2-TZVP(-f)/def2-TZV/J (un)restricted (open shell) DFT optimization calculations.

Occupation	**Bond character**	**MO number**
Occupied	π anti-bonding	167, 166, 161, 160, 157
	σ bonding	152, 149, 146, 144, 143, 141, 140, 138, 135
	π bonding	168, 164, 163, 162, 156, 154, 153, 151, 150, 148, 147
	π bonding/ π anti-bonding	165, 155
Unoccupied	σ anti-bonding	173, 170
	π anti-bonding	171,172

Table SI-2. The bond character of the MOs of lowest spin-state CoPPIX chloride according to the B3LYP/def2-TZVP(-f)/def2-TZV/J restricted DFT ground-state calculations.

For a detailed classification of the bonding structure between the cobalt centre and its nearest neighbours, all the MOs with bonding properties are inspected and the results are presented in Table SI-2. The orbitals prominent in the absorption process are either σ anti-bonding (LUMO, LUMO+3) or π anti-bonding (LUMO+1, LUMO+2) type. The corresponding bonding MOs are several occupied orbitals lying in the valence region. There are also a few occupied π anti-bonding orbitals but no σ-type anti-bonding orbital existing in the molecules. MOs 165 and 155 are particularly interesting because they show bonding

character on two adjacent nitrogen atoms while anti-bonding character on the other two. The unoccupied orbitals 188 and 189 exhibit a weak interaction between d_{xz} and d_{yz} of cobalt and nitrogen orbitals in the form of a weak π anti-bonding. This concludes our description of the local electronic structure on the Co sites of the porphyrin molecules which lacks π back-bonding hybridizations.

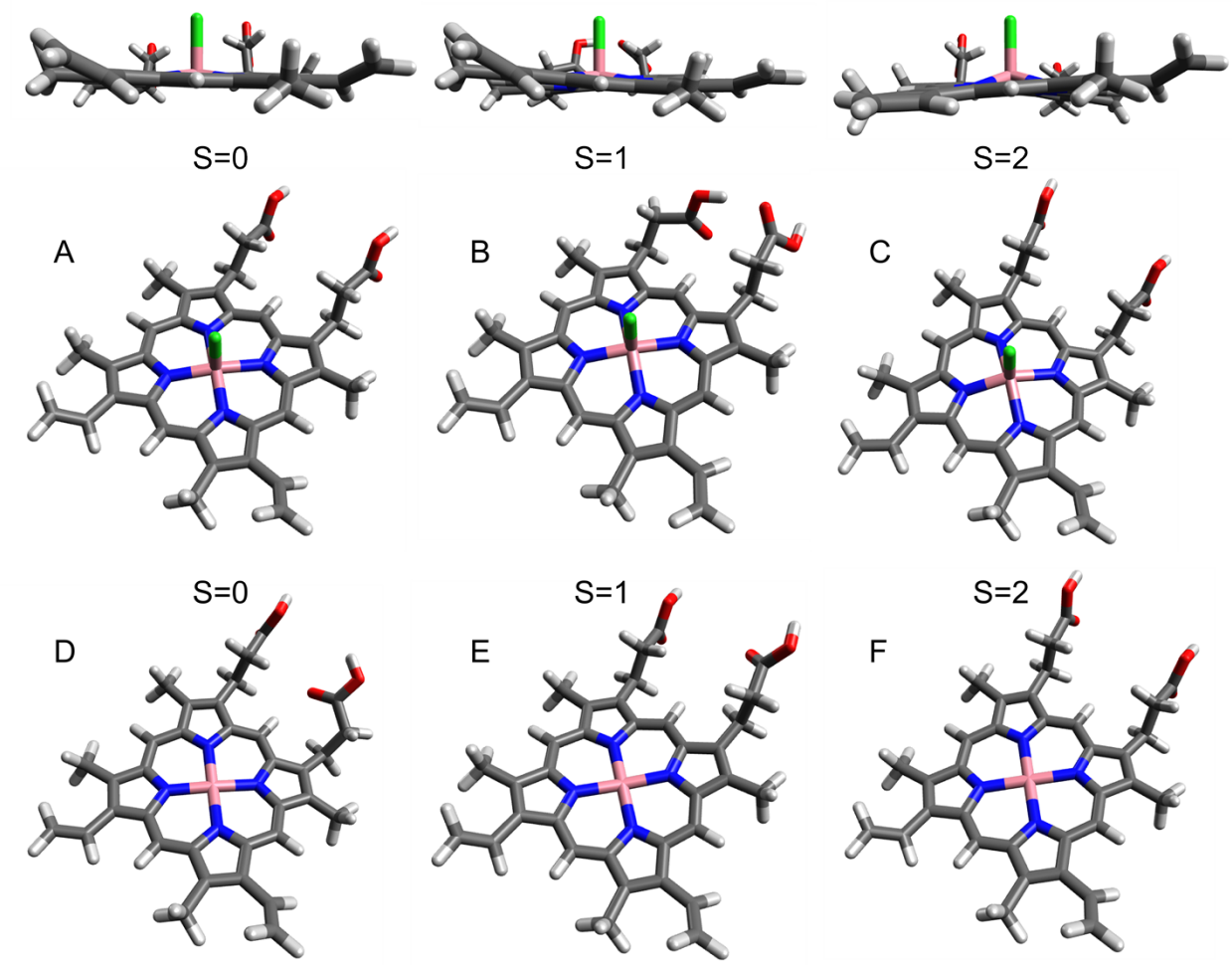

Figure SI-1. Molecular geometries of Co(III) protoporphyrin IX with (A-C) and without (D-F) a chloride bound to the cobalt center. Spin states are: S=0 (A), S=1 (B), S=2 (C), S=0 (D), S=1 (D), S=2 (F).

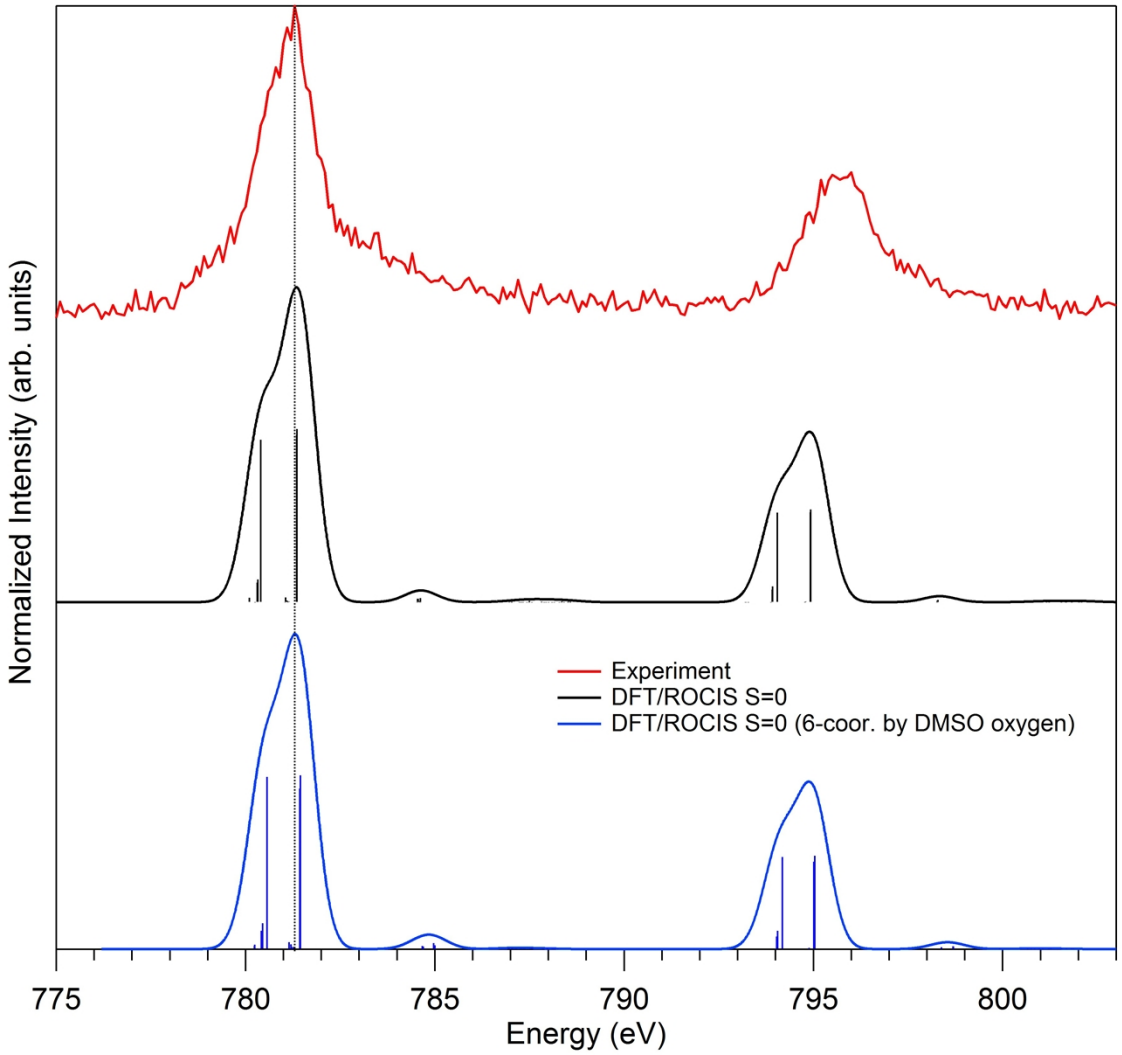

Figure SI-2. Experimental cobalt L-edge PFY spectrum of 50mM CoPPIX chloride solution in DMSO and DFT/ROCIS XA calculations for spin S = 0 for the 5- and 6-coordinated species. The 6th coordination is provided by the oxygen atom of dimethyl-sulfoxide. The computed spectra are shifted *ad hoc* by 16.35 eV (black trace) and 16.2 eV (blue trace).

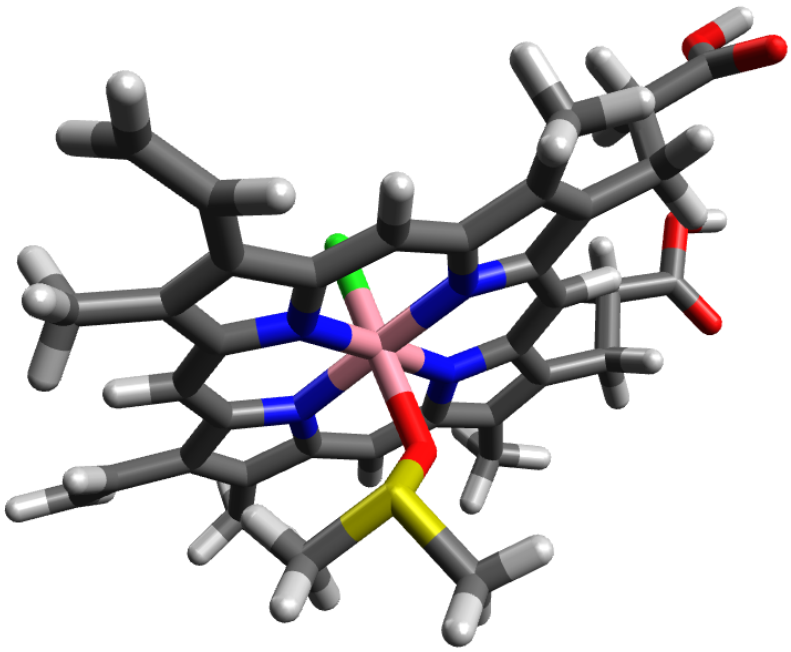

Figure SI-3. Molecular geometry of Co(III) protoporphyrin IX with DMSO oxygen in the cobalt's sixth-coordination site (S=0).

	DMSO-CoPP9-Cl S=0
Co-Cl bond distance (Å)	2.228
Co-N bond distance (Å)	1.996, 1.994, 2.009, 2.010
Co-O bond distance (Å)	2.117
Cl-Co-N bond angle (°)	91.3, 91.6, 90.8, 90.7
N-Co-N bond angle (°)	90.1, 89.9, 90.4, 89.5
Total dipole moment (Debye)	7.05
Total single point energy (eV)	-115118.24

Table SI-3. The coordination of cobalt in DMSO-CoPPIX-Cl according to the B3LYP/def2-TZVP(-f)/def2-TZV/J restricted DFT optimization calculations.