Consistent characterization of the electronic ground state of Iron (II) Phthalocyanine from valence and core-shell electron spectroscopy

Jonathan Laurent,[a] John Bozek,[b] Marc Briant,[c] Pierre Çarçabal,[a] Denis Cubaynes,[a] Aleksandar Milosavljević,[b] Ralph Püttner,[d] Niloufar Shafizadeh,[a] Marc Simon,[e] Benoit Soep,[a] and Gildas Goldsztejn*[a]

[a] Université Paris-Saclay, Institut des Sciences Moléculaires d'Orsay ISMO, UMR CNRS8214 F-91405 Orsay, France
[b] L'Orme des Merisiers, Synchrotron SOLEIL, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex, France
[c] Université Paris-Saclay, CEA, CNRS, LIDYL, 91191 Gif-sur-Yvette, France
[d] Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
[e] Sorbonne Université, CNRS, Laboratoire de Chimie Physique-Matière et Rayonnement, LCPMR, F-75005 Paris Cedex 05, France
*Corresponding author: gildas.goldsztejn@universite-paris-saclay.fr

Supplementary Information

Content

Table S1: Comparison between the distances, as defined in FiG. 1 of the main text, of the triplet electronic state calculated with the B3LYP functional as chosen in the main text, the singlet and quintuplet states with the same functional and the triplet state calculated with the B97D3 functional.

	Experimental values (Å)	B3LYP Triplet state	B3LYP Singlet state	B3LYP Quintuplet state	B97D3 Triplet state
a	1.927	1.948	1.951	1.949	1.944
b	1.378	1.374	1.373	1.377	1.385
c	1.322	1.318	1.319	1.323	1.322
d	1.450	1.452	1.453	1.454	1.454
e	1.395	1.401	1.400	1.401	1.410
f	1.392	1.391	1.391	1.388	1.395
g	1.390	1.388	1.388	1.391	1.394
h	1.394	1.403	1.403	1.400	1.408
δr	-	0.006	0.007	0.006	0.008
Δr_{max}	-	0.021	0.024	0.022	0.017

Figure S1: Experimental valence photoelectron spectrum (red line) and simulated DOS (black) of FePc along with the background photoelectron spectrum (in blue) mostly dominated by water and measured at hν = 57 eV. The two spectra were measured at the same oven temperature and with the same experimental resolution of ≈ 59 meV. The DOS was calculated for a triplet GS using the B3LYP functional and cc-pVTZ as a basis set.

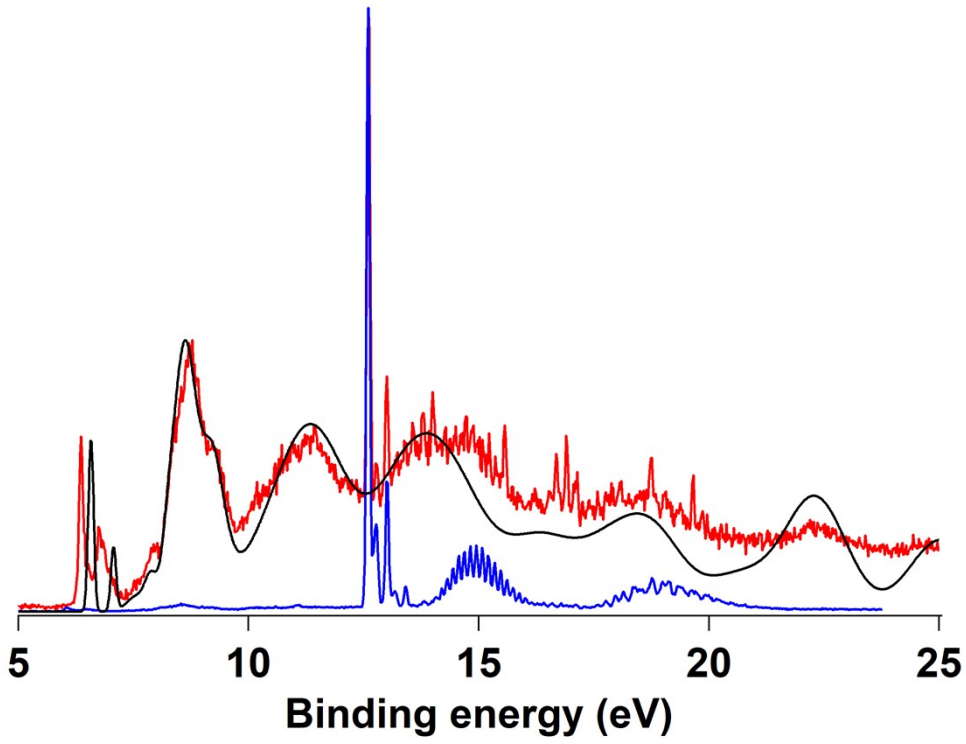

Figure S2: Experimental valence photoelectron spectrum (red dots) and simulated DOS for a triplet GS using the B3LYP functional (black line) and the B97D3 functional (blue line). In both case a triple-zeta polarized basis set was used.

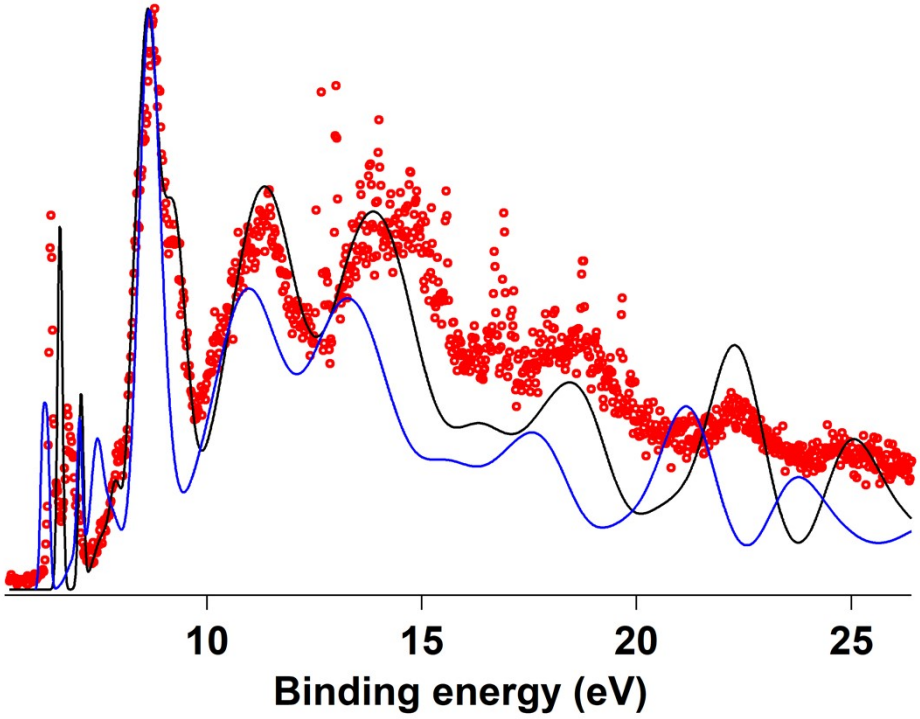

Figure S3: Experimental valence photoelectron spectrum (red dots) and simulated DOS spectra assuming a triplet (black line), a singlet (blue line), or a quintuplet (grey line) GS. At the B3LYP/cc-pVTZ level of theory.

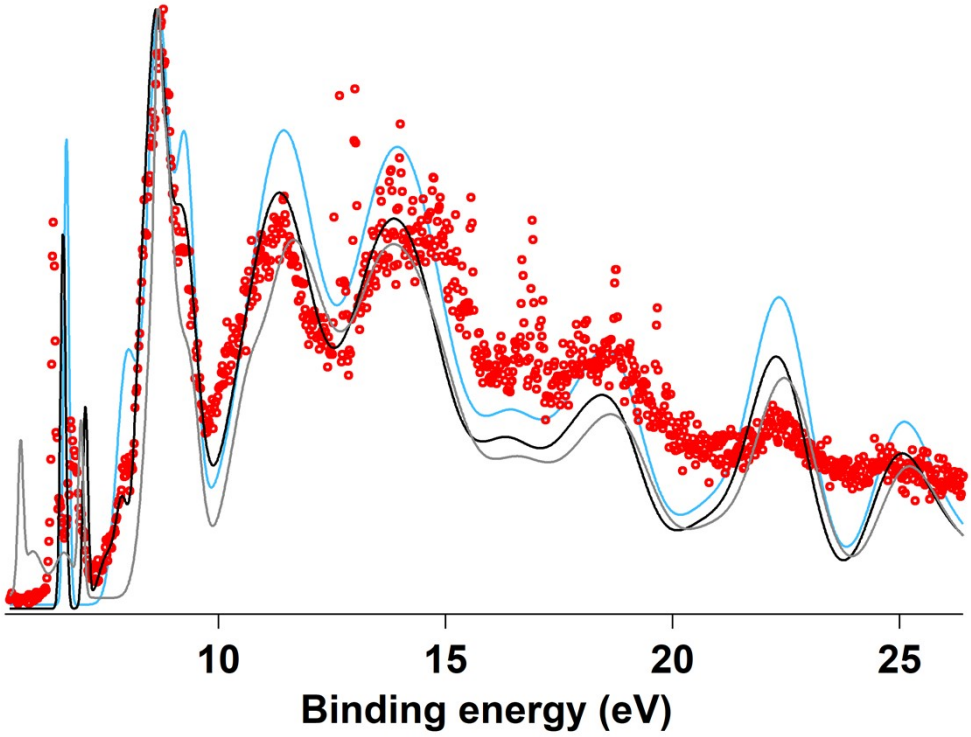

Table S2: B3LYP/cc-pVTZ optimized structure for the triplet state of FePc; xyz format, coordinates are given in Å.

H	7.468752000	-1.228599000	0.000000000
N	0.000000000	1.947736000	0.000000000
N	-1.947736000	0.000000000	0.000000000
N	0.000000000	-1.947736000	0.000000000
N	1.947736000	0.000000000	0.000000000
N	-2.376027000	2.376027000	0.000000000
N	-2.376027000	-2.376027000	0.000000000
N	2.376027000	-2.376027000	0.000000000
N	2.376027000	2.376027000	0.000000000
C	-1.113009000	2.754069000	0.000000000
C	-2.754069000	-1.113009000	0.000000000
C	1.113009000	-2.754069000	0.000000000
C	2.754069000	1.113009000	0.000000000
C	1.113009000	2.754069000	0.000000000
C	-2.754069000	1.113009000	0.000000000
C	-1.113009000	-2.754069000	0.000000000
C	2.754069000	-1.113009000	0.000000000
C	-0.700375000	4.146404000	0.000000000
C	-4.146404000	-0.700375000	0.000000000
C	0.700375000	-4.146404000	0.000000000
C	4.146404000	0.700375000	0.000000000
C	0.700375000	4.146404000	0.000000000
C	-4.146404000	0.700375000	0.000000000
C	-0.700375000	-4.146404000	0.000000000
C	4.146404000	-0.700375000	0.000000000
C	-1.419795000	5.336803000	0.000000000
C	-5.336803000	-1.419795000	0.000000000
C	1.419795000	-5.336803000	0.000000000
C	5.336803000	1.419795000	0.000000000
C	1.419795000	5.336803000	0.000000000
C	-5.336803000	1.419795000	0.000000000
C	-1.419795000	-5.336803000	0.000000000
C	5.336803000	-1.419795000	0.000000000
C	-0.701512000	6.524062000	0.000000000
C	-6.524062000	-0.701512000	0.000000000
C	0.701512000	-6.524062000	0.000000000
C	6.524062000	0.701512000	0.000000000
C	0.701512000	6.524062000	0.000000000
C	-6.524062000	0.701512000	0.000000000
C	-0.701512000	-6.524062000	0.000000000
C	6.524062000	-0.701512000	0.000000000
H	-2.500473000	5.328484000	0.000000000
H	-5.328484000	-2.500473000	0.000000000
H	2.500473000	-5.328484000	0.000000000
H	5.328484000	2.500473000	0.000000000
H	2.500473000	5.328484000	0.000000000
H	-5.328484000	2.500473000	0.000000000
H	-2.500473000	-5.328484000	0.000000000
H	5.328484000	-2.500473000	0.000000000

H	-1.228599000	7.468752000	0.000000000
H	1.228599000	7.468752000	0.000000000
H	-1.228599000	-7.468752000	0.000000000
H	1.228599000	-7.468752000	0.000000000
H	-7.468752000	-1.228599000	0.000000000
H	-7.468752000	1.228599000	0.000000000
H	7.468752000	1.228599000	0.000000000
Fe	0.000000000	0.000000000	0.000000000

Figure S4 : Experimental XPS spectrum at the Fe L2,3 edges measured (red dots) by Bidermane et al. (Reference 21 of the main text). The result of the CTM calculation for the first excited state, 3B2g, is plotted as a black solid line.