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Isolated molecule of Iron(II) phthalocyanine exhibits quintet ground-state: a nexus between theory and experiment

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Statement of the Problem: Iron(II) phthalocyanine (FePc), an important member of the phthalocyanines family has potential applications in the various fields, such as electrocatalysis, magnetic switching, electrochemical sensing, and phototheranostics. Inspite of the importance of electronic properties of FePc in such wide applications, a reliable determination of its ground-state is still challenging. Here we present combined state of the art computational methods and experimental approaches i. e. Mössbauer spectroscopy and SQUID magnetic measurements to identify the ground-state of FePc.

Methodology & Theoretical Orientation: The structures of FePc in different spin states have been obtained with various DFT functionals (B97-D3, BHLYP and B2-PLYP-D3). Multi-reference calculations have been performed using DFT optimized geometries. β-Iron(II)phthalocyanine (β-FePc) has been obtained from a commercial source. Chlorobenzene have been used for the ^{57}Fe Mössbauer spectroscopy measurements in the frozen state.

Findings: Depending on the functional, DFT calculations assign either quintet or, more frequently triplet, ground-state. At the CASSCF level the quintet is by 22.2 kcal/mol more stable with respect to triplet, which is reduced to 8.6 kcal/mol in subsequent perturbation treatment. The same ordering was also found using the DMRG approach. The hyperfine parameters of Mössbauer spectra confirm the quintet for isolated FePc frozen in the low-polarity solvent.

Conclusion & Significance: Multi-reference calculations clearly proved that the ground-state of the isolated FePc is quintet showing its larger stability with respect to the triplet ground-state previously favorized by DFT calculations. These conclusions perfectly correlate with experimental results based on Mössbauer spectroscopy and magnetic measurements of FePc frozen in chlorobenzene. In these conditions Fe(II)Pc behaves like in the gas-phase as verified by magnetic data.

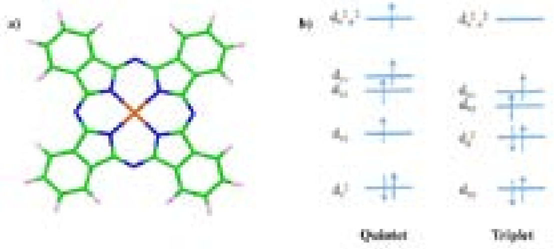

Figure 1: a) FePc (C-green, N-blue, Fe-red, H- pink), Fe-N distance is 2.008 Å (quintet) and 1.941 Å (triplet), and 1.926 Å (X-Ray experiment); b) the occupation of Fe(II) d-orbitals.

Recent Publications:

1. Trashin S et al. (2017) Singlet oxygen-based electrosensing by molecular photosensitizers Nat. Commun. 8:16108.
2. Filoti G, Kuz'min M D, Bartolomé J (2006) Mössbauer study of the hyperfine interactions and spin dynamics in α-iron(II) phthalocyanine. Phys. Rev. B 74: 134420.
3. Kirner J F, Dow W, Scheidt W R (1976) Molecular stereochemistry of two intermediate-spin complexes. Iron(II)

phthalocyanine and manganese(II) phthalocyanine. Inorg. Chem. 15(7):1685.

4. Berryman V E J, Boyd R J, Johnson E R (2015) Balancing exchange mixing in density-functional approximations for iron porphyrin. J. Chem. Theory Comput. 11(7):3022-3028.

Biography

Rabindranath Lo obtained his PhD in theoretical and computational chemistry from Central Salt & Marine Chemicals Research Instititute (CSIR) India. His is currently working as a Postdoctoral Fellow with Professor Pavel Hobza at the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic. His main research work focuses on theoretical and computational description of noncovalent interactions and their role in chemistry, bio disciplines and nanosciences. During his PhD studies, he worked on the strength and directionality of various halogen bonding, superbasicity and reactivation of acetylcholinesterase enzyme. Currently, he is working on the importance of non-covalent interactions to tune the electronic and magnetic properties of metal phthalocyanine complexes.

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