HERFD-XANES probes of electronic structures of iron$^{II/III}$ carbene complexes†

Meiyuan Guo[a,b], Om Prakash[c], Hao Fan[c], Lisa H. M. de Groot[c], Valtýr Freyr Hlynsson[c], Simon Kaufhold[c], Olga Gordivska[c], Nicolás Velásquez González[b], Pavel Chabera[b], Pieter Glatzel[d], Kenneth Wärnmark[c], Petter Persson[e], and Jens Uhlig *[b]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 200X

List of Figures

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

*Corresponding E-mail: jens.uhlig@chemphys.lu.se
[a] *College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P. R. China.*
[b] *Division of Chemical Physics, Chemical Center, Lund University, SE-221 00 Lund, Sweden.*
[c] *Center for Analysis and Synthesis (CAS), Department of Chemistry, Lund University, SE-22100 Lund, Sweden*
[d] *European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS 40220, 38043 Grenoble, France*
[e] *Division of Theoretical Chemistry, Chemical Center, Lund University, SE-221 00 Lund, Sweden*

References

1 P. Å. Malmqvist, K. Pierloot, A. R. M. Shahi, C. J. Cramer and L. Gagliardi, *J. Chem. Phys.*, 2008, **128**, 204109.
2 G. Ghigo, B. O. Roos and P.-Å. Malmqvist, *Chem. Phys. Lett*, 2004, **396**, 142–149.
3 N. Forsberg and P.-Å. Malmqvist, *Chem. Phys. Lett*, 1997, **274**, 196–204.

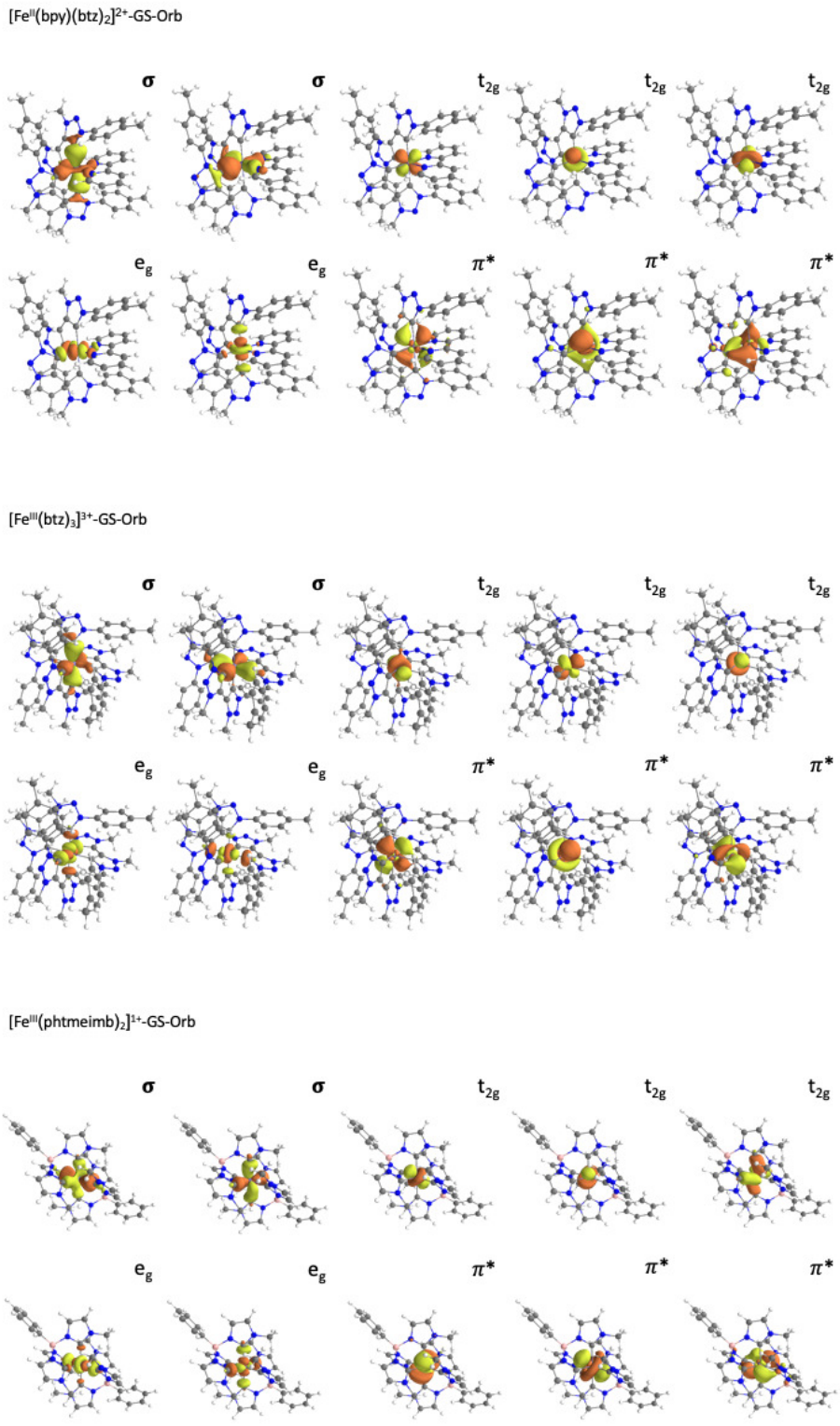

Fig. S1 The ground-state valence orbitals selected in the active space for $[Fe^{II}(bpy)(btz)_2]^{2+}$, $[Fe^{III}(btz)_3]^{3+}$ and $[Fe^{III}(phtmeimb)_2]^{1+}$.

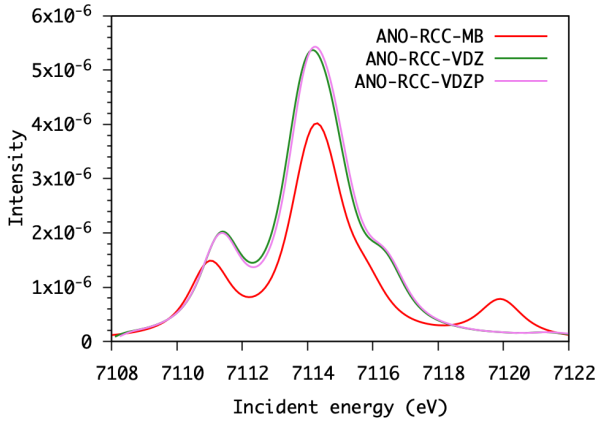

Fig. S2 The calculated K pre-edge XAS of $[Fe^{III}(phtmeimb)_2]^{1+}$ with basis set ANO-RCC-MB, ANO-RCC-VDZ and ANO-RCC-VDZP. The 40 core-excited states are included.

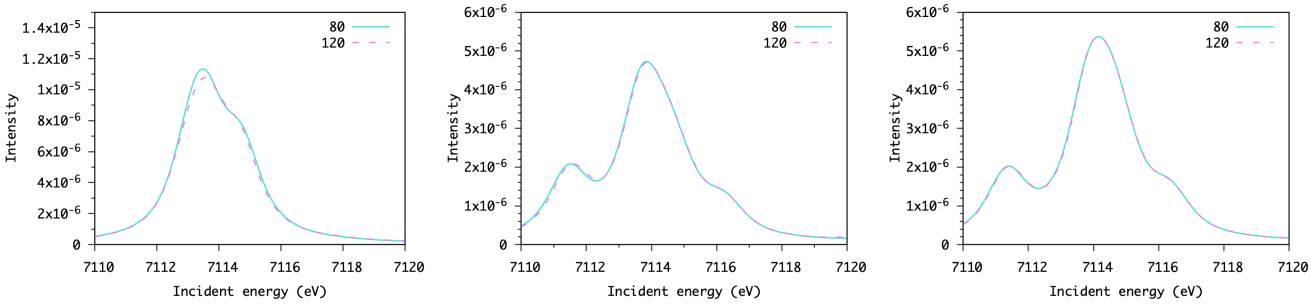

Fig. S3 The spectra calculated with 80 and 120 core-excited states for $[Fe^{II}(bpy)(btz)_2]^{2+}$(left), $[Fe^{III}(btz)_3]^{3+}$(middle) and $[Fe^{III}(phtmeimb)_2]^{1+}$(right).

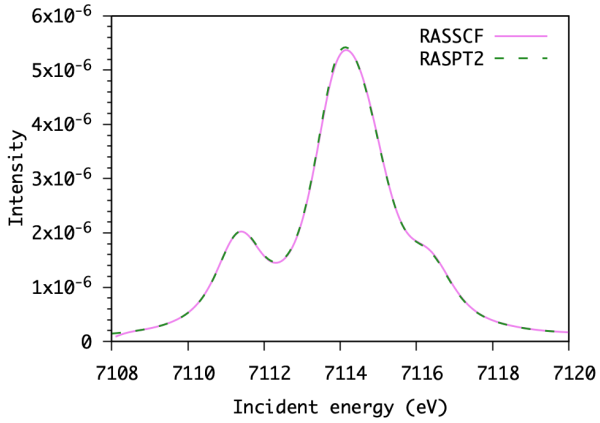

Fig. S4 The comparison between the RASSCF and RASPT2 spectrum of $[Fe^{III}(phtmeimb)_2]^{1+}$ with 40 core-excited states. RASPT2 calculations have been performed using multi-state (MS) RASPT2 [1] including all states from the RASSCF calculation. The default ionization-potential electron-affinity shift of 0.25 hartree has been used. [2] To reduce problems with intruder states an imaginary shift of 0.3 hartree has been applied throughout the calculations. [3]

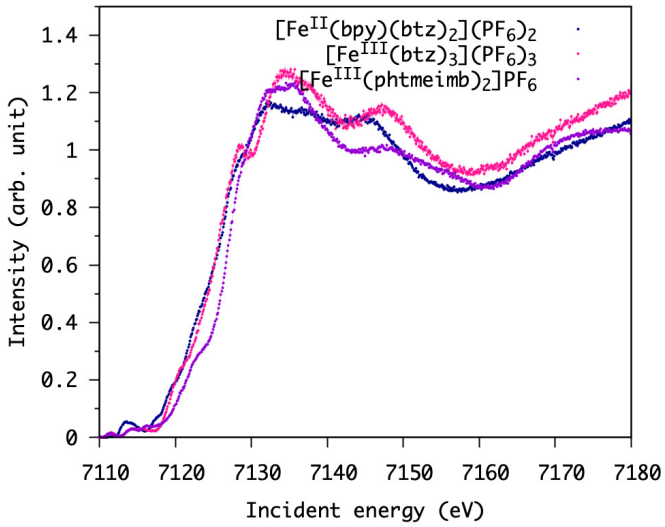

Fig. S5 The experimental iron full HERFD-XAS spectra of $[Fe^{II}(bpy)(btz)_2](PF_6)_2$, $[Fe^{III}(btz)_3](PF_6)_3$ and $[Fe^{III}(phtmeimb)_2]PF_6$. The data was normalized to one at 7129.3 eV. The normalization can have an effect on the relative height of the pre-edge features. From the statistical error size and precision with which we can estimate this normalization factor we estimate that this procedure adds approximately 1% of the measured signal at this position to the error. In this plot we give the 2-σ error marginals as derived from the combination of statistical fluctuation or the measurement/shot noise and the above mentioned estimated normalization error.

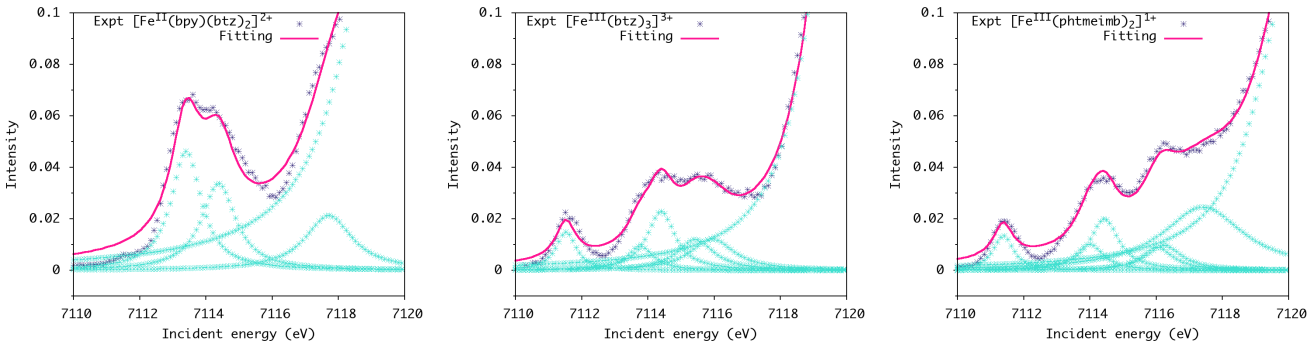

Fig. S6 The peak fitting for the metal K edge XAS in the energy range from 7110 to 7120 eV. Fitting of K pre-edge features was performed using the EDG-FIT module of the EXAFSPAK suite using pseudo-Voigt line shapes with a fixed 50:50 ratio of Lorentzian to Gaussian functions where the peak positions, width and intensities were varied.