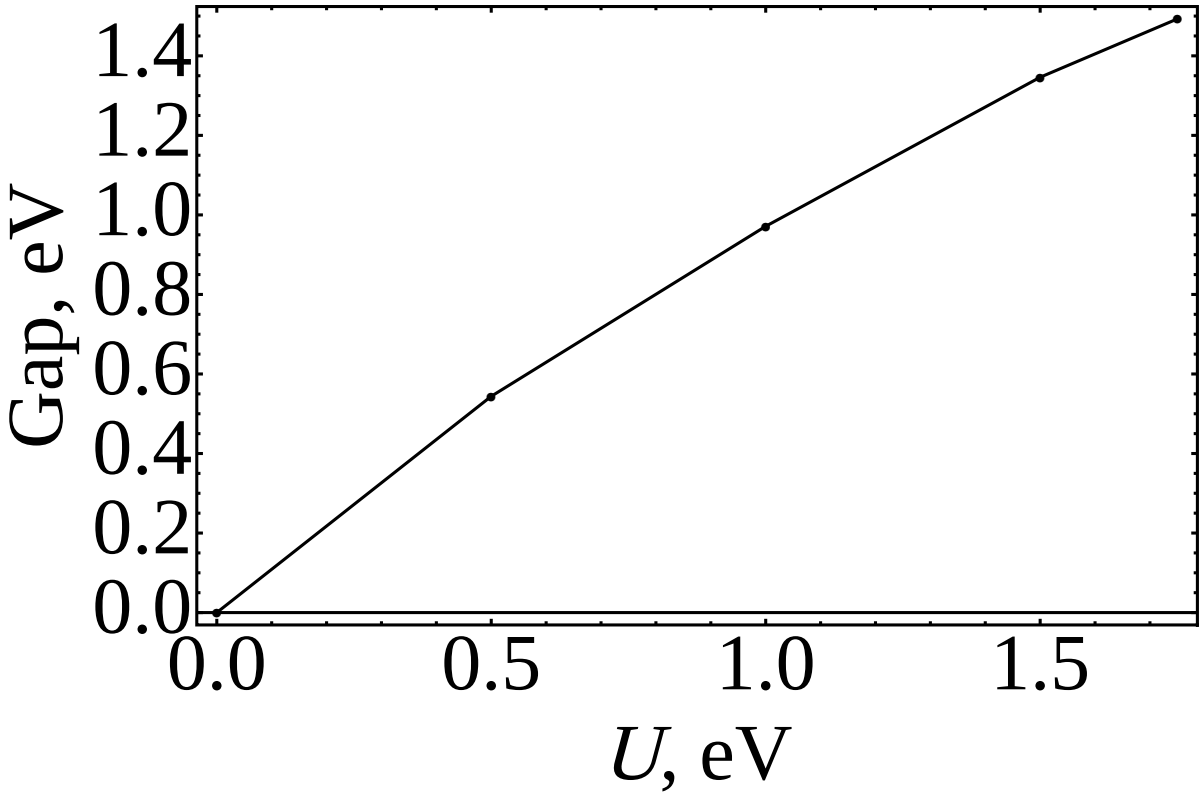
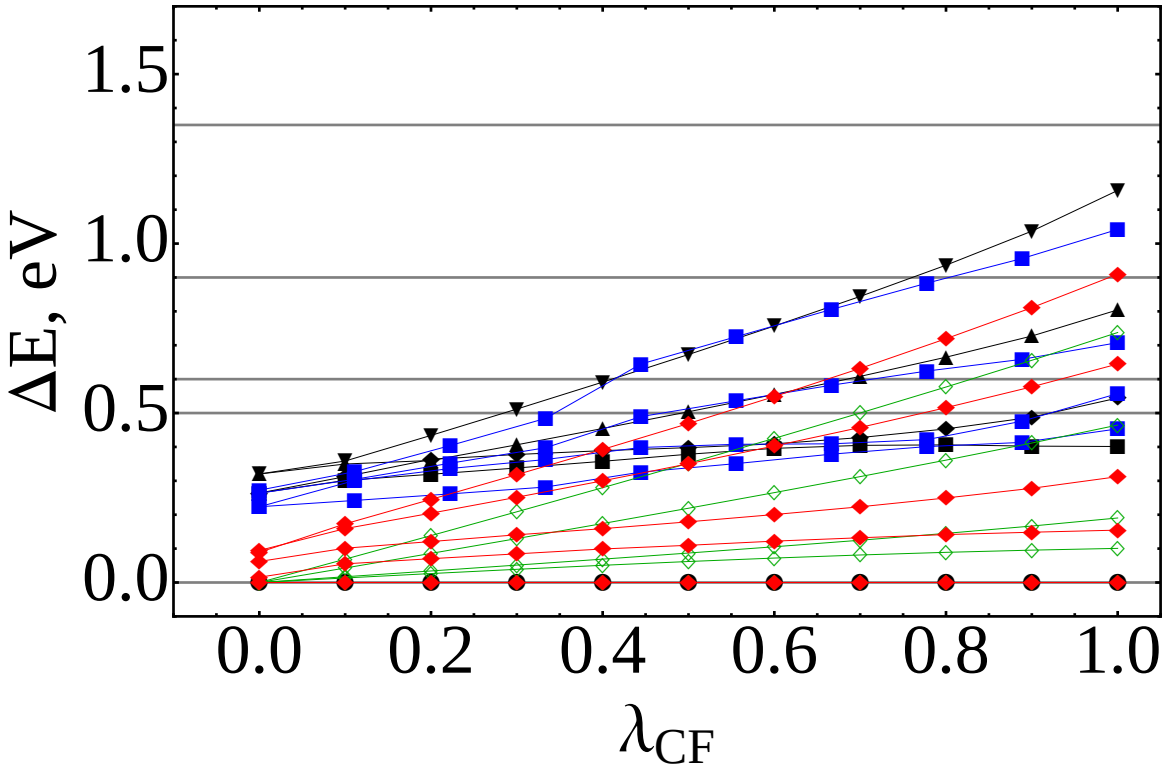
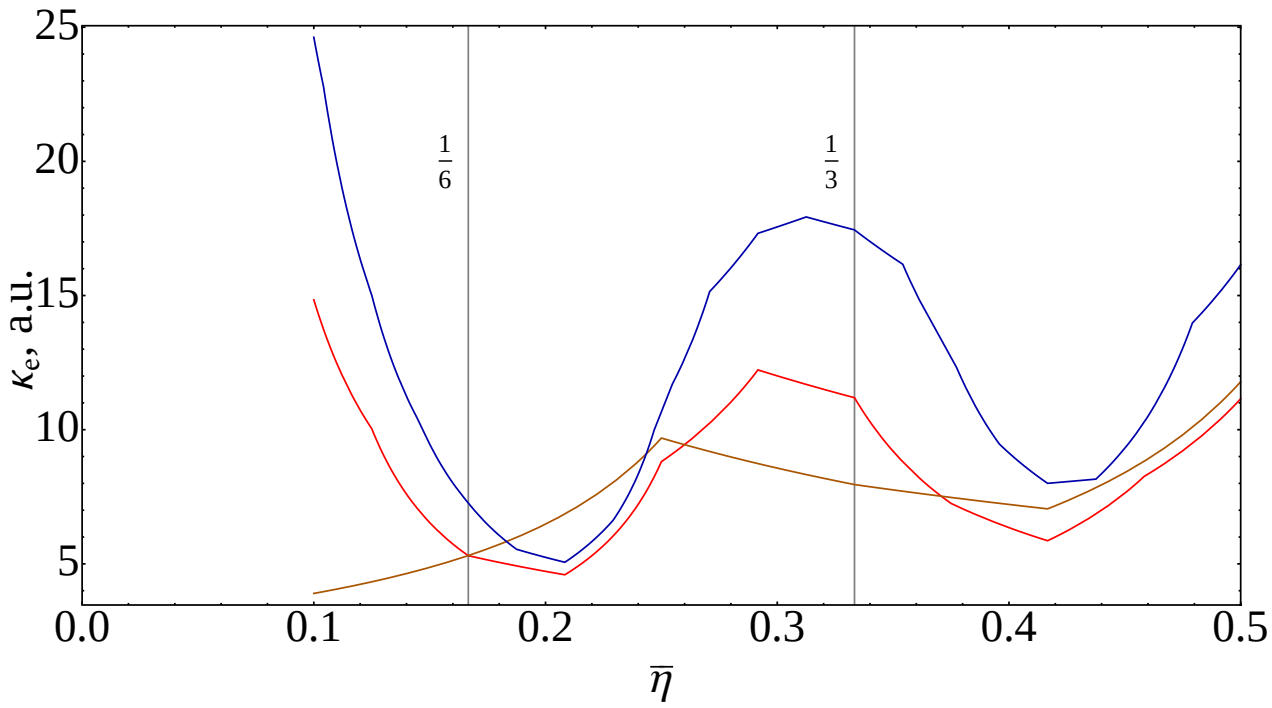


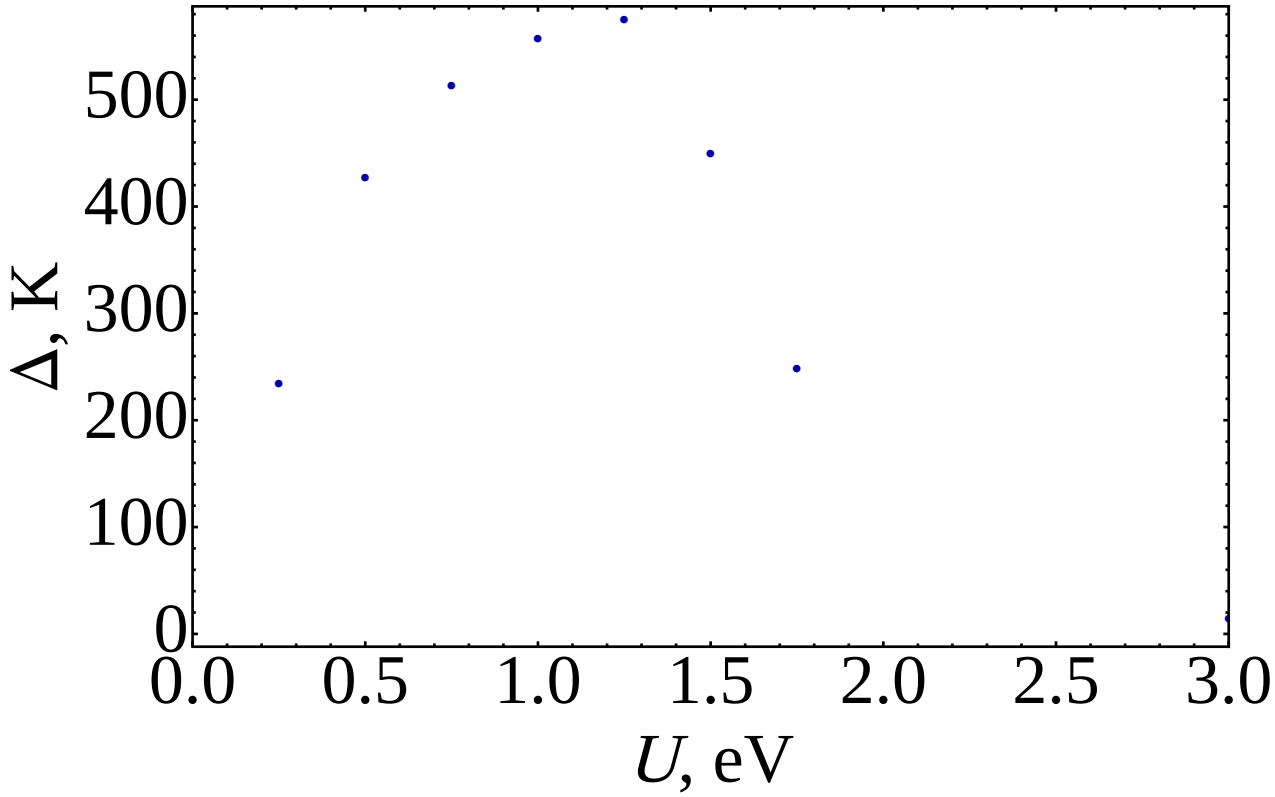
Supplementary Figure 1. **The mean field PW91+U band gap in** Fe_2(DOBDC) **vs. the on-site electron repulsion** U**.**



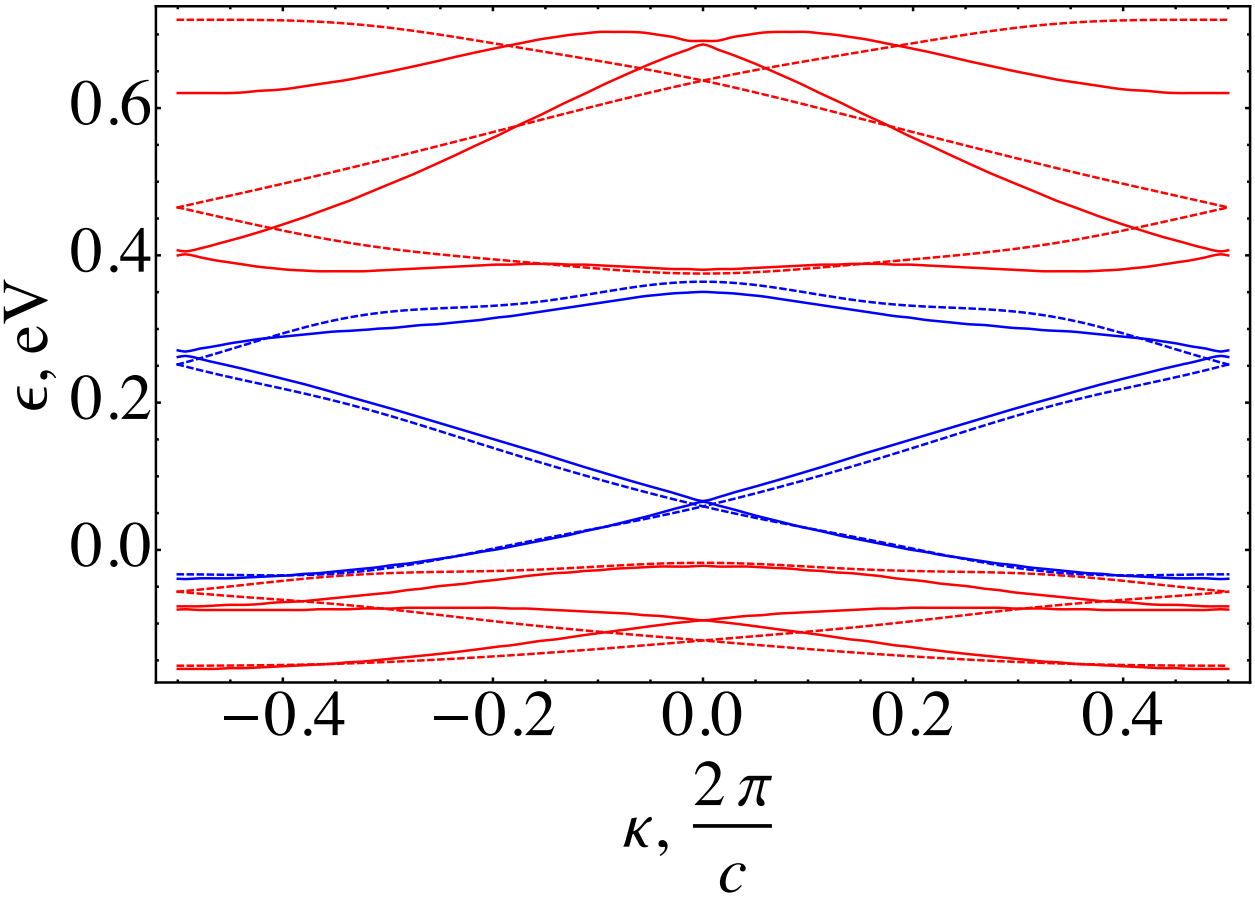
Supplementary Figure 2. **The crystal field splitting of ^5D microstates in the scaled crystal field $\lambda_{\mathrm{CF}}H_{\mathrm{CF}}$ as a function of the coupling constant λ_{CF}.** The excitation energies are computed in the CIS(D) (black triangles), TD-DFT (blue squares), CASSCF (green diamonds), CASSCF MP2 (red diamonds), approximations. The horizontal lines are the transitions observed in the UV/vis spectrum[1]. The approximate TD-DFT and CIS(D) give similar results. CASSCF, which omits dynamic electron correlation, underestimates the splittings. The dynamic correlation is partially accounted for in CASSCF MP2.



Supplementary Figure 3. **The charge compressibility** κ_e **vs.** $\bar{\eta}$ **for** $U = 0.5$ **eV and for the chains of** 24 **(blue),** 48 **(red), and** 96 **(brown)** Fe **sites.**



Supplementary Figure 4. **The charge gap computed with the DMRG vs. the electron repulsion** U**.**



Supplementary Figure 5. **Comparison of the PW91+U band structure at $U = 0$ (solid lines) and the three-band tight binding model(dashed lines) for the a_0- and a_1-derived d-bands for the wavevector κ along the trigonal direction $Z\Lambda\Gamma\Lambda Z$.**

Multiplet	Leading configuration	CASSCF	MP2	TD-DFT	CIS(D)
$[Fe-O_2]^{2+}\ ^7A_0$	$a_0^1a_1^1a_2^1a_3^1a_4^1(\pi')^2(\pi'')^1$	0	0	0	
$[Fe-O_2]^{2+}\ ^7A_1$	$a_0^1a_1^1a_2^1a_3^1a_4^1(\pi')^1(\pi'')^2$	0.74	1.28	1.31	

Supplementary Table 1. **Excited states in** $[Fe-O_2]^{2+}$**.** The vertical excitation energies (in eV) and the leading configurations in CASSCF wavefunctions for the ground and first excited states in $[Fe-O_2]^{2+}$. All the methods agree on the nature of the first excited state.

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[1]E. D. Bloch, L. J. Murray, W. L. Queen, S. Chavan, S. N. Maximoff, J. P. Bigi, R. Krishna, V. K. Peterson, F. Grandjean, G. J. Long, B. Smit, S. Bordiga, C. M. Brown, and J. R. Long, "Selective binding of O_2 over N_2 in a redox-active metal-organic framework with open iron(II) coordination sites," J. Am. Chem. Soc. **133**, 14814–14822 (2011).