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Supporting Information for

Theoretical Investigation of Tetrahedral Distortion of Four-Coordinate Iron(II) Centres in $FePd(CN)_4$

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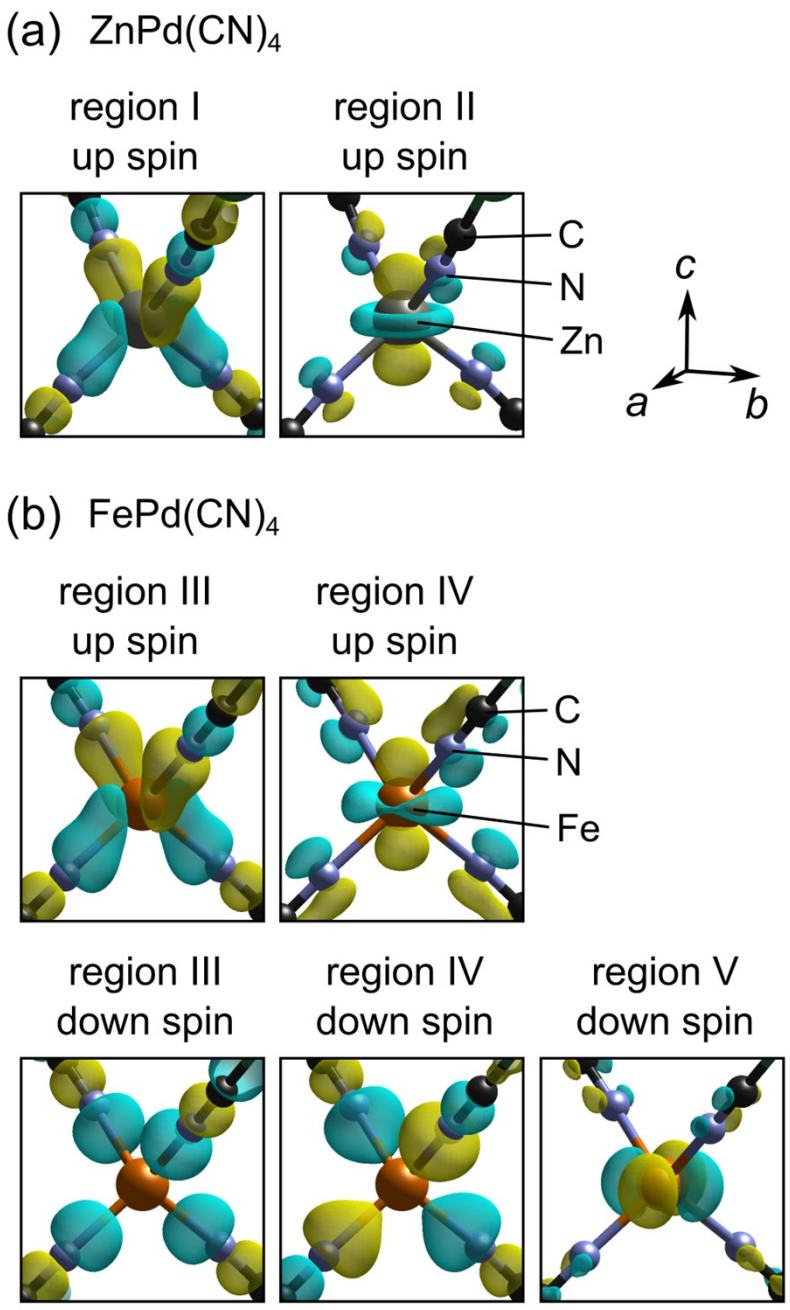

Figure S1. Examples of charge density isosurfaces of a band at Γ point in each energy region for (a) $ZnPd(CN)_4$ and (b) $FePd(CN)_4$. The energy regions are given in Fig. 3. The charge densities were multiplied by the sign (phase) of the wave function (yellow and blue). The isosurfaces correspond to 0.01 $Å^{-3}$.

Supplementary Discussion

Figure S1 shows examples of the charge density isosurfaces of a band in each energy region. The energy regions from I to V correspond to (I) t_2 and (II) e orbitals for $ZnPd(CN)_4$, and (III) t_2, (IV) d_{z^2} and (V) $d_{x^2-y^2}$ orbitals for $FePd(CN)_4$, respectively (see also Fig. 3). The charge densities were multiplied by the positive or negative sign of the corresponding wave function using pymatgen,[1] to show the bonding or anti-bonding nature of bands. In Fig. S1, bands at Γ point are plotted as representative examples. It should be noted that Fig. S1 shows the charge densities of specific bands at Γ point while Fig. 4 shows the total charge densities of all the occupied bands at multiple k-points sampled in the Brillouin zone.

In up-spin bands at regions I and III, there are high charge densities with the same sign between N and metal ions, demonstrating the bonding nature between 2s and 2p orbitals of N and 3d t_2 orbitals of metal ions. On the other hand, in up-spin bands at regions II and IV, 2p orbitals of N and 3d d_{z^2} orbitals of metal ions exhibit the same sign, but the interatomic charge densities are very low. This indicates the non-bonding or weak interactions between them. In down-spin bands at regions III and IV, N 2s and 2p orbitals do not form the bonds between Fe orbitals, as there are no energy states of Fe down-spin electrons in the energy regions. Fe 3d $d_{x^2-y^2}$ orbital is highly localized around Fe ion, as found from a down-spin band at region V. No anti-bonding states between N and metal ions were observed for the bands at Γ point.

References:

1. S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, S. Cholia, D. Gunter, V. L. Chevrier, K. A. Persson and G. Ceder, *Comput. Mater. Sci.*, 2013, **68**, 314–319.