A combined ligand field and density functional theory analysis of the magnetic anisotropy in oligonuclear complexes based on Fe^{III}-CN-M^{II} exchange-coupled pairs

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Supplementary Material

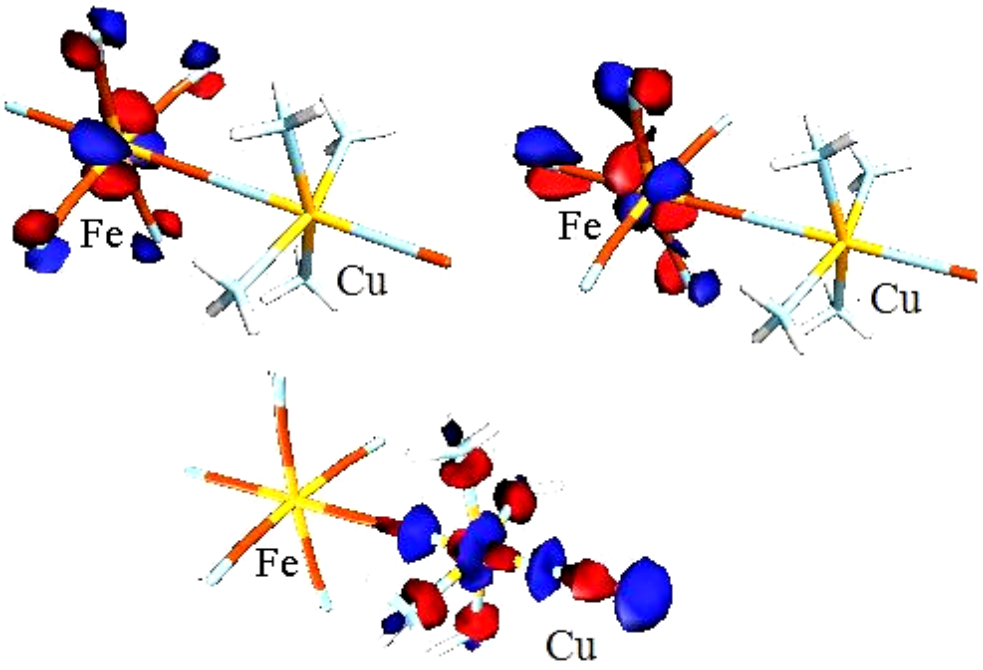

Figure S.1 The magnetic orbitals in the $^2B_1$ ($e^4b_2^1$) and ^2E ($e^3b_2^2$) states of $[Fe(CN)_6]^{3-}$ (top), and of the $^2A_1$ (d_{z2}) ground state of $[Cu(NH_3)_4NC]^{1+}$ (bottom) from broken symmetry DFT calculations using a B1LYP functional.

Full Derivation of the Hamiltonian of the Fe^{III}-CN-Cu^{II} Pair

The matrix of exchange Hamiltonian $-J_{ij}\hat{\mathbf{s}}_i\hat{\mathbf{s}}_j$, with i and j denoting the magnetic orbitals on center 1 and 2, within the spin only basis $\alpha_i\alpha_j$, $\beta_i\alpha_j$, $\alpha_i\beta_j$ and $\beta_i\beta_j$ is given by:

$$\mathbf{H}_{\mathbf{exc}}(i,j) = \begin{array}{c} \begin{matrix} \alpha_i\alpha_j & \beta_i\alpha_j & \alpha_i\beta_j & \beta_i\beta_j \end{matrix} \\ \begin{bmatrix} -\frac{1}{4}J_{ij} & 0 & 0 & 0 \\ 0 & \frac{1}{4}J_{ij} & -\frac{1}{2}J_{ij} & 0 \\ 0 & -\frac{1}{2}J_{ij} & \frac{1}{4}J_{ij} & 0 \\ 0 & 0 & 0 & -\frac{1}{4}J_{ij} \end{bmatrix} \end{array} \qquad \text{(S.1)}$$

The operator $\hat{H}_{SO} = \varsigma_1\hat{\mathbf{l}}_1\hat{\mathbf{s}}_1$ of the spin-orbit coupling interaction of $[Fe(CN)_6]^{3-}$ is represented within the t_{2g} $(\xi,\eta,\zeta)\alpha$ and $(\xi,\eta,\zeta)\beta$ spin-orbital basis as follows (the spin-orbit coupling constant ζ is defined as positive for Fe^{III}):

$$\mathbf{H_{so}} = \begin{array}{c} \begin{matrix} \xi\alpha_1 & \eta\alpha_1 & \zeta\alpha_1 & \xi\beta_1 & \eta\beta_1 & \zeta\beta_1 \end{matrix} \\ \begin{bmatrix} 0 & -\frac{i}{2}\zeta & 0 & 0 & 0 & \frac{1}{2}\zeta \\ \frac{i}{2}\zeta & 0 & 0 & 0 & 0 & -\frac{i}{2}\zeta \\ 0 & 0 & 0 & -\frac{1}{2}\zeta & \frac{i}{2}\zeta & 0 \\ 0 & 0 & -\frac{1}{2}\zeta & 0 & \frac{i}{2}\zeta & 0 \\ 0 & 0 & -\frac{i}{2}\zeta & -\frac{i}{2}\zeta & 0 & 0 \\ \frac{1}{2}\zeta & \frac{i}{2}\zeta & 0 & 0 & 0 & 0 \end{bmatrix} \end{array} \qquad \text{(S.2)}$$

Combining eqs S1, S2 with the Jahn-Teller Hamiltonian (eq.3), we arrive at the total Hamiltonian (S.3), represented by the product of the spin-orbit basis of Fe^{III} and the spin-only basis of Cu^{II} α',β':

$[(\xi,\eta,\zeta)\alpha_1 ; (\xi,\eta,\zeta)\beta_1]\ \alpha'$ and $[(\xi,\eta,\zeta)\alpha_1 ; (\xi,\eta,\zeta)\beta_1]\ \beta'$:

$$
\mathbf{H} = \begin{array}{c}
\begin{matrix} (\xi,\alpha_1)\alpha' & (\eta\alpha_1)\alpha' & (\zeta\alpha_1)\alpha' & (\xi,\beta_1)\alpha' & (\eta\beta_1)\,\alpha' & (\zeta\beta_1)\,\alpha' & (\xi,\alpha_1)\,\beta' & (\eta\alpha_1)\,\beta' & (\zeta\alpha_1)\,\beta' & (\xi,\beta_1)\,\beta' & (\eta\beta_1)\,\beta' & (\zeta\beta_1)\,\beta' \end{matrix} \\
\begin{bmatrix}
-\frac{J(^2E)}{4} & -\frac{i}{2}\varsigma - V_\tau Q_\zeta & -V_\tau Q_\eta & 0 & 0 & \frac{1}{2}\varsigma & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{i}{2}\varsigma - V_\tau Q_\varsigma & -\frac{J(^2E)}{4} & -V_\tau Q_\xi & 0 & 0 & -\frac{i}{2}\varsigma & 0 & 0 & 0 & 0 & 0 & 0 \\
-V_\tau Q_\eta & -V_\tau Q_\xi & -\frac{J(^2B_2)}{4} & -\frac{1}{2}\varsigma & \frac{i}{2}\varsigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{1}{2}\varsigma & \frac{J(^2E)}{4} & \frac{i}{2}\varsigma - V_\tau Q_\varsigma & -V_\tau Q_\eta & -\frac{J(^2E)}{2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\frac{i}{2}\varsigma & -\frac{i}{2}\varsigma - V_\tau Q_\varsigma & \frac{J(^2E)}{4} & -V_\tau Q_\xi & 0 & -\frac{J(^2E)}{2} & 0 & 0 & 0 & 0 \\
\frac{1}{2}\varsigma & \frac{i}{2}\varsigma & 0 & -V_\tau Q_\eta & -V_\tau Q_\xi & \frac{J(^2B_2)}{4} & 0 & 0 & -\frac{J(^2B_2)}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & -\frac{J(^2E)}{2} & 0 & 0 & \frac{J(^2E)}{4} & -\frac{i}{2}\varsigma - V_\tau Q_\zeta & -V_\tau Q_\eta & 0 & 0 & \frac{1}{2}\varsigma \\
0 & 0 & 0 & 0 & -\frac{J(^2E)}{2} & 0 & \frac{i}{2}\varsigma - V_\tau Q_\zeta & \frac{J(^2E)}{4} & -V_\tau Q_\xi & 0 & 0 & -\frac{i}{2}\varsigma \\
0 & 0 & 0 & 0 & 0 & -\frac{J(^2B_2)}{2} & -V_\tau Q_\eta & -V_\tau Q_\xi & \frac{J(^2B_2)}{4} & -\frac{1}{2}\varsigma & \frac{i}{2}\varsigma & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{2}\varsigma & -\frac{J(^2E)}{4} & \frac{i}{2}\varsigma - V_\tau Q_\zeta & -V_\tau Q_\eta \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{i}{2}\varsigma & -\frac{i}{2}\varsigma - V_\tau Q_\zeta & -\frac{J(^2E)}{4} & -V_\tau Q_\xi \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2}\varsigma & \frac{i}{2}\varsigma & 0 & -V_\tau Q_\eta & -V_\tau Q_\xi & -\frac{J(^2B_2)}{4}
\end{bmatrix}
\end{array}
\qquad \text{(S.3)}
$$

We now focus on the particular case of a Fe^{III}-CN-Cu^{II} pair of C_{4v} symmetry with no Jahn-Teller distortions on $[Fe(CN)_6]^{3-}$. We make use of the eigenfunctions of $\mathbf{H_{SO}}$ in the form given in reference [90] of the manuscript. E"(α",β") and U'(μ,ν,κ,λ), defined by the column vectors **c**(i) (i=α", β",μ, ν, κ, λ), lead to the following matrix, which transforms $\mathbf{H_{SO}}$ (eq.S.2) into this basis:

$$[\mathbf{c}(\alpha") \;\; \mathbf{c}(\beta") \;\; \mathbf{c}(\mu) \;\; \mathbf{c}(\nu) \;\; \mathbf{c}(\kappa) \;\; \mathbf{c}(\lambda)] =$$

$$= \mathbf{T} = \begin{bmatrix} 0 & \frac{i}{\sqrt{3}} & -\frac{i}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{6}} & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{6}} & 0 \\ \frac{i}{\sqrt{3}} & 0 & 0 & -i\sqrt{\frac{2}{3}} & 0 & 0 \\ \frac{i}{\sqrt{3}} & 0 & 0 & \frac{i}{\sqrt{6}} & 0 & \frac{i}{\sqrt{2}} \\ -\frac{1}{\sqrt{3}} & 0 & 0 & -\frac{1}{\sqrt{6}} & 0 & \frac{1}{\sqrt{2}} \\ 0 & -\frac{i}{\sqrt{3}} & 0 & 0 & -i\sqrt{\frac{2}{3}} & 0 \end{bmatrix} \qquad \text{(S.4)}$$

The transformed matrix $\mathbf{T'H_{SO}T}$ is diagonal with eigenvalues -ζ[E"(α",β")] and ζ/2[U'(μ,ν,κ,λ)] and with a Zeeman Hamiltonian in the z direction [i.e. $\hat{H}_{Z2} = \mu_B(\mathbf{s}_{z1} + k\mathbf{l}_{1z})B_z$], given by (S.5) and with an effective M_s' value of each of the components of E"(α",β") and U'(μ,ν,κ,λ) as indicated.

	α"	β"	μ	ν	κ	λ
M_s'=	1/2	-1/2	3/2	1/2	-1/2	-3/2

$$\mathbf{H}^{\mathbf{z}}_{\mathbf{Z1}} = \mu_B B_z \begin{bmatrix} -\frac{1}{3}-\frac{2}{3}k & 0 & 0 & -\frac{\sqrt{2}}{3}(2+k) & 0 & 0 \\ 0 & \frac{1}{3}+\frac{2}{3}k & 0 & 0 & 0 & 0 \\ 0 & 0 & 1-k & 0 & 0 & 0 \\ -\frac{\sqrt{2}}{3}(2+k) & 0 & 0 & \frac{1}{3}-\frac{1}{3}k & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{3}+\frac{1}{3}k & 0 \\ 0 & 0 & 0 & 0 & 0 & -1+k \end{bmatrix} \qquad \text{(S.5)}$$

The Fe^{III} [E"(α",β"), M_s'=±1/2, U'(μ,ν,κ,λ); M_s'=±3/2, ±1/2,] - Cu^{II} [α',β'(m_s=±1/2)] pair states, can then easily be classified according to the total $M_s=M_s'\pm m_s$ value. Using eq.S.4, **H** can be reduced to a block diagonal form, and utilizing the C_{4v} symmetry, we arrive at the symmetry-adapted functions of the Fe-Cu pair states and the corresponding energy expressions:

M_s=±2: E U'

M_s=+2 μ,α'
M_s=-2 λ,β'

$$\mathbf{H}(E)=\frac{1}{2}\zeta-\frac{1}{4}J(^2E) \qquad \text{(S.6)}$$

M_s=±1: E:

	E"	U'	U'
+1	α"α'	να'	μβ'
-1	β"β'	κβ'	λα'

$$\mathbf{H}(E)=\begin{bmatrix} -\zeta+\frac{1}{6}J(^2E)-\frac{1}{12}J(^2B_2) & \pm\frac{1}{6\sqrt{2}}[J(^2E)+J(^2B_2)] & \pm\frac{1}{\sqrt{6}}J(^2E) \\ \pm\frac{1}{6\sqrt{2}}[J(^2E)+J(^2B_2)] & \frac{1}{2}\zeta+\frac{1}{12}J(^2E)-\frac{1}{6}J(^2B_2) & \frac{1}{2\sqrt{3}}J(^2E) \\ \pm\frac{1}{\sqrt{6}}J(^2E) & \frac{1}{2\sqrt{3}}J(^2E) & \frac{1}{2}\zeta+\frac{1}{4}J(^2E) \end{bmatrix} \qquad \text{(S.7)}$$

M_s=0:

$$B_1(\mathrm{E}'')=\frac{1}{\sqrt{2}}(-\beta''\alpha'+\alpha''\beta') \quad B_1(\mathrm{U}')=\frac{1}{\sqrt{2}}(\kappa\alpha'+\nu\beta')$$

$$\mathbf{H}(B_1)=\begin{bmatrix} -\zeta-\frac{1}{8}J(^2E)-\frac{1}{12}J(^2B_2) & \frac{1}{6\sqrt{2}}[-J(^2E)+J(^2B_2)] \\ \frac{1}{6\sqrt{2}}[-J(^2E)+J(^2B_2)] & \frac{1}{2}\zeta-\frac{1}{12}J(^2E)-\frac{1}{6}J(^2B_2) \end{bmatrix} \qquad \text{(S.8)}$$

$$B_2(\mathrm{E}'')=\frac{1}{\sqrt{2}}(\beta''\alpha'+\alpha''\beta') \quad B_2(\mathrm{U}')=\frac{1}{\sqrt{2}}(\kappa\alpha'-\nu\beta')$$

$$\mathbf{H}(B_2)=\begin{bmatrix} -\zeta-\frac{1}{8}J(^2E)+\frac{1}{4}J(^2B_2) & \frac{1}{2\sqrt{2}}[J(^2E)+J(^2B_2)] \\ \frac{1}{2\sqrt{2}}[J(^2E)+J(^2B_2)] & \frac{1}{2}\zeta-\frac{1}{12}J(^2E)+\frac{1}{2}J(^2B_2) \end{bmatrix} \qquad \text{(S.9)}$$

As follows from (S.8) and (S.9), there is configuration mixing between the pair of states of lowest energy $B_1(\mathrm{E}'')$, $B_2(\mathrm{E}'')$ and $B_1(\mathrm{U}')$, $B_2(\mathrm{U}')$. Using perturbation theory we obtain

eq.S.10-S.11 for the second order energy change, where exchange terms in the denominator have been neglected. With the values of $J(^2E)$ =19, $J(^2B_2)$ =1.6

$$\Delta E[B_1(\Gamma_7)] = -\frac{1}{108}\frac{[J(^2B_2) - J(^2E)]^2}{\zeta} \qquad \text{(S.10)}$$

$$\Delta E[B_2(\Gamma_7)] = -\frac{1}{12}\frac{[J(^2B_2) + J(^2E)]^2}{\zeta} \qquad \text{(S.11)}$$

and ζ =345 (all in cm^{-1}) we obtain $\Delta E[B_1(E'')]$ = -0.008 cm^{-1} and $\Delta E[B_2(E'')]$ = -0.106 cm^{-1}, that is negligible influence on the ground state spin levels from the Fe^{III}(U') - Cu^{II} excited spin states.

The energies of the lowest four spin states, which arise from Fe^{III}(E")- Cu^{II} exchange coupling, are given by (as derived in reference [19] in the manuscript and the Supporting Information [1]):

$$\mathbf{H}_{Fe(\Gamma_7)Cu} = \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} \frac{1}{6}J(^2E) - \frac{1}{12}J(^2B_2) & 0 & 0 & -\frac{1}{3}\delta J(^2E) \\ 0 & -\frac{1}{6}J(^2E) + \frac{1}{12}J(^2B_2) & \frac{1}{6}J(^2B_2) & 0 \\ 0 & \frac{1}{6}J(^2B_2) & -\frac{1}{6}J(^2E) + \frac{1}{12}J(^2B_2) & 0 \\ -\frac{1}{3}\delta J(^2E) & 0 & 0 & \frac{1}{6}J(^2E) - \frac{1}{12}J(^2B_2) \end{bmatrix} \end{array} \qquad \text{(S.12)}$$

with $\delta J(^2E)$ to account for the possible decrease of symmetry $C_{4v} \rightarrow C_{2v}$:

$$\delta J(^2E) = \frac{J_{\xi\xi} - J_{\eta\eta}}{2} \qquad \text{(S.13)}$$

$$J(^2E) = \frac{J_{\xi\xi} + J_{\eta\eta}}{2} \qquad \text{(S.14)}$$

The parameters J, D and E in the spin Hamiltonian $\hat{H}_{sph}$ (S.15, i.e. a simplified form of eq.4) are derived by comparing S.12 with the representation of $\hat{H}_{sph}$ using the basis $\alpha''\alpha'$ $\beta''\alpha', \alpha''\beta', \beta''\beta'$;

$$\hat{H}_{sph} = -J\mathbf{s_1'}\mathbf{s_2} + \frac{2D}{3}(2\mathbf{s_{1z}'}\mathbf{s_{2z}} - \mathbf{s_{1x}'}\mathbf{s_{2x}} - \mathbf{s_{1y}'}\mathbf{s_{2y}}) + 2E(\mathbf{s_{1x}'}\mathbf{s_{2x}} - \mathbf{s_{1y}'}\mathbf{s_{2y}}) \qquad \text{(S.15)}$$

$$\mathbf{H}_{\mathbf{sph}} = \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} -\frac{1}{4}J+\frac{1}{3}D & 0 & 0 & E \\ 0 & \frac{1}{4}J-\frac{1}{3}D & -\frac{1}{2}J-\frac{1}{3}D & 0 \\ 0 & -\frac{1}{2}J-\frac{1}{3}D & \frac{1}{4}J-\frac{1}{3}D & 0 \\ E & 0 & 0 & -\frac{1}{4}J+\frac{1}{3}D \end{bmatrix} \end{array} \qquad \text{(S.16)}$$

In going from (S.15) to (S.16) we make use of the following substitutions:

$$-\mathbf{s}_1'\mathbf{s}_2 \Rightarrow \begin{bmatrix} -\frac{1}{4} & 0 & 0 & 0 \\ 0 & \frac{1}{4} & -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} & \frac{1}{4} & 0 \\ 0 & 0 & 0 & -\frac{1}{4} \end{bmatrix}; \qquad \text{(S.17)}$$

$$2\mathbf{s}_{1z}'\mathbf{s}_{2z} - \mathbf{s}_{1x}'\mathbf{s}_{2x} - \mathbf{s}_{1y}'\mathbf{s}_{2y} \Rightarrow \begin{bmatrix} \frac{1}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & -\frac{1}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} \end{bmatrix} \qquad \text{(S.18)}$$

$$\mathbf{s}_{1x}'\mathbf{s}_{2x} - \mathbf{s}_{1y}'\mathbf{s}_{2y} = \begin{bmatrix} 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \frac{1}{2} & 0 & 0 & 0 \end{bmatrix} \qquad \text{(S.19)}$$

These can be derived, using the direct products $\mathbf{s}_i \otimes \mathbf{s}_j$ (i,j=x,y,z) of the spinmatrices for s=1/2

$$\mathbf{s_x} = \frac{1}{2}\begin{bmatrix} \alpha & \beta \\ 0 & 1 \\ 1 & 0 \end{bmatrix}; \mathbf{s}_y = \frac{i}{2}\begin{bmatrix} \alpha & \beta \\ 0 & -1 \\ 1 & 0 \end{bmatrix}; \mathbf{s_z} = \frac{1}{2}\begin{bmatrix} \alpha & \beta \\ 1 & 0 \\ 0 & -1 \end{bmatrix}; \quad \text{(S.20)}$$

$$-\frac{1}{4}J + \frac{1}{3}D = \frac{1}{6}J\left(^2E\right) - \frac{1}{12}J(^2B_2) \quad \text{(S.21)}$$

$$-\frac{1}{2}J - \frac{1}{3}D = \frac{1}{6}J(^2B_2) \quad \text{(S.22)}$$

$$E = -\frac{1}{3}\delta J(^2E) \quad \text{(S.23)}$$

From (S.21) and (S.22) result the expressions of J and D (eq.14).

Is it always possible to derive the parameters of the spin Hamiltonian from first principle calculations? There is a configuration mixing between the spin multiplets due to the E"-Cu^{II} and the multiplets due to the U'-Cu^{II} interaction via exchange coupling terms. In the discussed example, $\zeta >> J\left(^2E\right),\ J(^2B_2)$ and the parameters J,D and E (S.21-S.23) can be uniquely determined. However, starting from Fe^{III}-CN-Cu^{II} with a C_{4v} geometry and octahedral $[Fe(CN)_6]^{3-}$, and introducing a D_{3d} Jahn-Teller distortion U' splits and starts to mix with E". In Figure S.2, we plot the electronic energy levels of $[Fe(CN)_6]^{3-}$ in dependence of the ratio $V_\tau Q_\tau/\zeta$ [obtained by diagonalization of the Hamiltonian S.3 with $J(^2E)=J(^2B_2)=0$]. It follows, that the electronic ground state is well separated from the excited states both in O_h and in the distorted D_{3d} geometries. One can understand this result if one transforms the spin-orbit coupling matrix into the trigonal basis of eq.S.24.

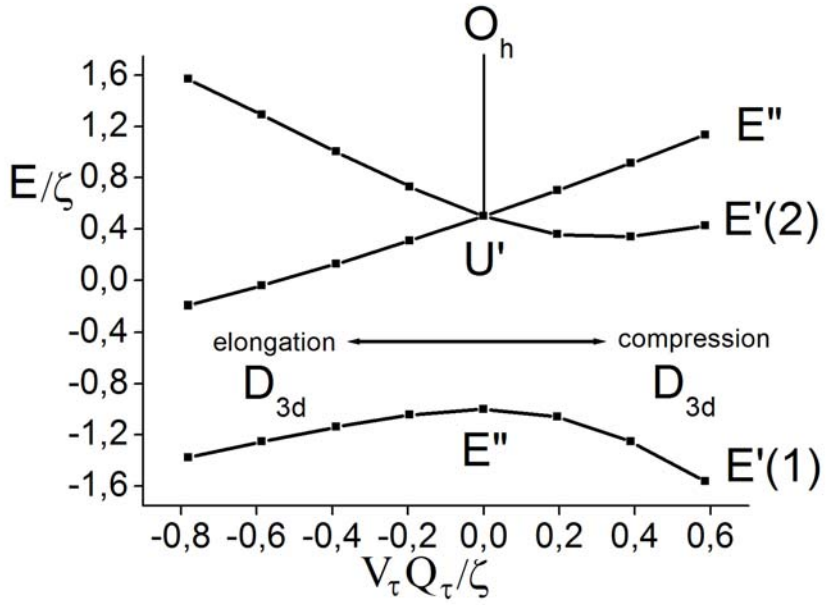

Figure S.2. Electronic levels of $[Fe(CN)_6]^{3-}$ in dependence of the vibronic coupling energy in units of ζ.

In this basis, $\mathbf{H_{JT}}$ is diagonal with the energies of $^2A_1$ and ^2E, given by $-2V_\tau Q_\tau$ and $V_\tau Q_\tau$, respectively.

$$\varphi(A_1) = \frac{1}{\sqrt{3}}(\xi + \eta + \zeta)$$
$$\varphi(Ey) = \frac{1}{\sqrt{2}}(\xi - \eta) \qquad \text{(S.24)}$$
$$\varphi(Ex) = \frac{1}{\sqrt{6}}(-\xi - \eta + 2\zeta)$$

While $^2A_1$ is the ground state for trigonally compressed geometries, it is of ^2E symmetry in elongated geometries. However the ^2E term spits to first order by spin-orbit coupling with an energy difference between the ground state E'(1) and the E" lowest excited state given by ζ. It is again much larger than J(^2E) and J($^2B_2$). Therefore, one can safely apply the spin-Hamitonian (eq.4) and deduce its parameters by comparison with the eigenvalues of eq.(1) in the whole range of Jahn-Teller-distorted geometries between Q_τ= -0.256 and -0.256Å. In the given example (Table 5, Q_τ= 0.128 Å for Fe-Cu) one first diagonalizes $\mathbf{H_{SO}}$+$\mathbf{H_{JT}}$, including the Zeeman matrix with a small magnetic field (B_z=0.0001 T), providing the proper components α" and β" of the

ground state Kramers doublet E'(1) (Figure S.2). With the resulting eigenvectors, one transforms the Hamiltonian (eq.S.3), yielding the following traceless matrix (with energies in cm^{-1}) of the ground state spin levels:

$$\mathbf{H_{sph}} = \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} 3.038 & 0.615 & 0.200(-1+i) & -2.933(1-i) \\ 0.615 & -3.038 & 0.020(-1+i) & 0.200(1-i) \\ 0.200(-1-i) & 0.020(-1-i) & -3.038 & -0.615 \\ -2.933(1+i) & 0.200(1+i) & -0.615 & 3.038 \end{bmatrix} \end{array} \quad \text{(S.25)}$$

One can show, using simple manipulations (as described e.g. by eq.S.15-S.20), that within the $\alpha''\alpha'$, $\beta''\alpha'$, $\alpha''\beta'$ and $\beta''\beta'$ basis, the spin-Hamiltonian of eq.4 leads to the matrix representation given by eq. S.26. From the comparison of S.25 and S.26 the spin-Hamiltonian parameters of Fe-Cu from Table 5 has been obtained (entry for Q_τ= 0.128 Å).

Finally, within the spin-only basis and without distortions on $[Fe(CN)_6]^{3-}$, the Zeeman operator $\hat{H}_{Z1}$ is represented by the matrices given in eq.S.27-S.29, showing directly the coupling of the local g-tensors of Fe^{III} and Cu^{II}.

$$\mathbf{H_{sph}} = \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} \frac{1}{3}D-\frac{1}{4}J & \frac{1}{4}(D_{xz}-iD_{yz}-iA_x-A_y) & \frac{1}{4}(D_{xz}-iD_{yz}+iA_x+A_y) & E-\frac{1}{2}iD_{xy} \\ \frac{1}{4}(D_{xz}+iD_{yz}+iA_x-A_y) & -\frac{1}{3}D+\frac{1}{4}J & -\frac{1}{3}D-\frac{1}{2}J-\frac{i}{2}A_z & \frac{1}{4}(-D_{xz}+iD_{yz}-iA_x-A_y) \\ \frac{1}{4}(D_{xz}+iD_{yz}-iA_x+A_y) & -\frac{1}{3}D-\frac{1}{2}J+\frac{i}{2}A_z & -\frac{1}{3}D+\frac{1}{4}J & \frac{1}{4}(-D_{xz}+iD_{yz}+iA_x+A_y) \\ E+\frac{1}{2}iD_{xy} & \frac{1}{4}(-D_{xz}-iD_{yz}+iA_x-A_y) & \frac{1}{4}(-D_{xz}-iD_{yz}-iA_x+A_y) & \frac{1}{3}D-\frac{1}{4}J \end{bmatrix} \end{array} \quad \text{(S.26)}$$

$$\mathbf{H^x_{Z1}} = \mu_B B_x \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} 0 & -\frac{1}{3}-\frac{2}{3}k & \frac{1}{2}g_{2x} & 0 \\ -\frac{1}{3}-\frac{2}{3}k & 0 & 0 & \frac{1}{2}g_{2x} \\ \frac{1}{2}g_{2x} & 0 & 0 & -\frac{1}{3}-\frac{2}{3}k \\ 0 & \frac{1}{2}g_{2x} & -\frac{1}{3}-\frac{2}{3}k & 0 \end{bmatrix} \end{array} \quad \text{(S.27)}$$

$$\mathbf{H}^{\mathbf{y}}_{\mathbf{Z1}} = \mu_B B_y \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} 0 & \frac{i}{3}+\frac{2i}{3}k & -\frac{i}{2}g_{2y} & 0 \\ -\frac{i}{3}-\frac{2i}{3}k & 0 & 0 & -\frac{i}{2}g_{2y} \\ \frac{i}{2}g_{2y} & 0 & 0 & \frac{i}{3}+\frac{2i}{3}k \\ 0 & \frac{i}{2}g_{2y} & -\frac{i}{3}-\frac{2i}{3}k & 0 \end{bmatrix} \end{array} \qquad \text{(S.28)}$$

$$\mathbf{H}^{z}_{\mathbf{Z1}} = \mu_B B_z \begin{array}{c} \begin{matrix} \alpha''\alpha' & \beta''\alpha' & \alpha''\beta' & \beta''\beta' \end{matrix} \\ \begin{bmatrix} -\frac{1}{3}-\frac{2}{3}k+\frac{1}{2}g_{2z} & 0 & 0 & 0 \\ 0 & \frac{1}{3}+\frac{2}{3}k+\frac{1}{2}g_{2z} & 0 & 0 \\ 0 & 0 & -\frac{1}{3}-\frac{2}{3}k-\frac{1}{2}g_{2z} & 0 \\ 0 & 0 & 0 & \frac{1}{3}+\frac{2}{3}k-\frac{1}{2}g_{2z} \end{bmatrix} \end{array} \qquad \text{(S.29)}$$

The Hamiltonian and the z component of the Zeeman matrix for the Fe^{III}-CN-Ni^{II} Pair

Applying consistently the same procedure as for the Fe^{III}-Cu^{II} pair, we have derived the matrix of the Hamiltonian (eq.1) which results from the spin coupling between $[Fe(CN)_6]^{3-}$ and the S=1 (M_s=±1,0) ground state of Ni^{II} for a binuclear unit with C_{4v} symmetry. Restricting to the manifold of the six spin states pertaining to the coupling of the $[Fe(CN)_6]^{3-}$ in its ground state E" and the S=1 state of Ni^{II} , we list the energy matrix in eq. S.30 and the z component of the Zeeman matrix in eq.31. Exchange coupling parameters have already been specified for the Fe^{III}-Cu^{II} pair, D_{Ni} is the zero-field splitting parameter of Ni^{II}. We notice, that in the ground (excited) E"(1) [E"(2)] spin states D_{Ni} is added (subtracted) from the diagonal energy term, thus leading to an increase (decrease) of the spin energy gap for negative (positive) values of D_{Ni}. Taking the difference between the diagonal matrix elements, i.e. E(α",0; β",0)-E(α",-1; β",1) eq.18 is derived.

As in the case of the Fe^{III}-Cu^{II} pair, spin Hamiltonian theory is applicable for the Fe^{III}-Ni^{II} spin-cluster of a general C_s symmetry, and the parameters of eq.4 can be derived from a comparison between the (traceless) 6x6 energy matrix (eq.S.32, Q_τ= 0.128 Å) and the spin Hamiltonian, written in the parametric form of eq.S.33. Numerical values are listed in Table 5.

Finally g-tensor values of the Fe^{III}-Cu^{II} and Fe^{III}-Ni^{II} with bistable ground states listed in Table 9 have been calculated using a well documented procedure (reference [87] of the manuscript).

$$\mathbf{H} = \begin{array}{c} \begin{matrix} \alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \end{matrix} \\ \begin{bmatrix} \frac{1}{3}J(^2E)-\frac{1}{6}J(^2B_2)+\frac{1}{3}D_{Ni} & 0 & 0 & -\frac{\sqrt{2}}{3}\delta J(^2E) & 0 & 0 \\ 0 & -\frac{1}{3}J(^2E)+\frac{1}{6}J(^2B_2)+\frac{1}{3}D_{Ni} & \frac{1}{3\sqrt{2}}J(^2B_2) & 0 & 0 & 0 \\ 0 & \frac{1}{3\sqrt{2}}J(^2B_2) & -\frac{2}{3}D_{Ni} & 0 & 0 & -\frac{\sqrt{2}}{3}\delta J(^2E) \\ -\frac{\sqrt{2}}{3}\delta J(^2E) & 0 & 0 & -\frac{2}{3}D_{Ni} & \frac{1}{3\sqrt{2}}J(^2B_2) & 0 \\ 0 & 0 & 0 & \frac{1}{3\sqrt{2}}J(^2B_2) & -\frac{1}{3}J(^2E)+\frac{1}{6}J(^2B_2)+\frac{1}{3}D_{Ni} & 0 \\ 0 & 0 & -\frac{\sqrt{2}}{3}\delta J(^2E) & 0 & 0 & \frac{1}{3}J(^2E)-\frac{1}{6}J(^2B_2)+\frac{1}{3}D_{Ni} \end{bmatrix} \end{array} \quad \text{(S.30)}$$

$$\mathbf{H}^{\mathbf{z}}_{\mathbf{Z1}} = \begin{array}{c} \begin{matrix} \alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \end{matrix} \\ \begin{bmatrix} -\frac{1}{3}-\frac{2}{3}k+g_{z2} & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{3}+\frac{2}{3}k+g_{z2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{3}-\frac{2}{3}k & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{3}+\frac{2}{3}k & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{3}-\frac{2}{3}k-g_{z2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{3}+\frac{2}{3}k-g_{z2} \end{bmatrix} \end{array} \quad \text{(S.31)}$$

$$\mathbf{H}_{\mathbf{sph}} = \begin{array}{c} \begin{matrix} \alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \end{matrix} \\ \begin{bmatrix} 4.039 & 0.995 & 0.0995(-1+i) & -2.669(1-i) & 0 & 0 \\ 0.995 & -4.039 & -0.107(1-i) & 0.0995(1-i) & 0 & 0 \\ 0.0995(-1-i) & -0.107(1+i) & 0 & 0 & -0.0995(1-i) & -2.669(1-i) \\ -2.669(1+i) & 0.0995(1+i) & 0 & 0 & -0.107(1-i) & 0.0995(1-i) \\ 0 & 0 & -0.0995(1+i) & -0.107(1+i) & -4.039 & -0.995 \\ 0 & 0 & -2.669(1+i) & 0.0995(1+i) & -0.995 & 4.039 \end{bmatrix} \end{array} \quad \text{(S.32)}$$

$$\mathbf{H}_{\mathbf{sph}} = \begin{array}{c} \begin{matrix} \alpha'',1 & \beta'',1 & \alpha'',0 & \beta'',0 & \alpha'',-1 & \beta'',-1 \end{matrix} \\ \begin{bmatrix} \frac{2}{3}D-\frac{1}{2}J & \frac{1}{2}(D_{xz}-iD_{yz}-iA_x-A_y) & \frac{1}{2\sqrt{2}}(D_{xz}-iD_{yz}+iA_x+A_y) & \sqrt{2}E-\frac{i}{\sqrt{2}}D_{xy} & 0 & 0 \\ \frac{1}{2}(D_{xz}+iD_{yz}+iA_x-A_y) & -\frac{2}{3}D+\frac{1}{2}J & -\frac{\sqrt{2}}{3}D-\frac{1}{\sqrt{2}}J-\frac{i}{\sqrt{2}}A_z & \frac{1}{2\sqrt{2}}(-D_{xz}+iD_{yz}-iA_x-A_y) & 0 & 0 \\ \frac{1}{2\sqrt{2}}(D_{xz}+iD_{yz}-iA_x+A_y) & -\frac{\sqrt{2}}{3}D-\frac{1}{\sqrt{2}}J+\frac{i}{\sqrt{2}}A_z & 0 & 0 & \frac{1}{2\sqrt{2}}(D_{xz}-iD_{yz}+iA_x+A_y) & \sqrt{2}E-\frac{i}{\sqrt{2}}D_{xy} \\ \sqrt{2}E+\frac{i}{\sqrt{2}}D_{xy} & \frac{1}{2\sqrt{2}}(-D_{xz}-iD_{yz}+iA_x-A_y) & 0 & 0 & -\frac{\sqrt{2}}{3}D-\frac{1}{\sqrt{2}}J-\frac{i}{\sqrt{2}}A_z & \frac{1}{2\sqrt{2}}(-D_{xz}+iD_{yz}-iA_x-A_y) \\ 0 & 0 & \frac{1}{2\sqrt{2}}(D_{xz}+iD_{yz}-iA_x+A_y) & -\frac{\sqrt{2}}{3}D-\frac{1}{\sqrt{2}}J+\frac{i}{\sqrt{2}}A_z & -\frac{2}{3}D+\frac{1}{2}J & \frac{1}{2}(-D_{xz}+iD_{yz}+iA_x+A_y) \\ 0 & 0 & \sqrt{2}E+\frac{i}{\sqrt{2}}D_{xy} & \frac{1}{2\sqrt{2}}(-D_{xz}-iD_{yz}+iA_x-A_y) & \frac{1}{2}(-D_{xz}-iD_{yz}-iA_x+A_y) & \frac{2}{3}D-\frac{1}{2}J \end{bmatrix} \end{array} \quad \text{(S.33)}$$

Dynamic Jahn-Teller Coupling

Since the Fe^{III}-CN bond is stronger than the Cu^{II}-NC and Ni^{II}-NC bonds, we can restrict vibronic coupling to the $[Fe(CN)_6]^{3-}$ unit and consider only the τ_{2g} mode for its vibronic levels. One can readily extend eq.1 with the nuclear kinetic and potential energy operators (eq.S.34); $\hbar\omega_\tau$ is the energy of the three-dimensional harmonic oscillator

$$\hat{H}_{vib} = \frac{1}{2}\hbar\omega_\tau(\hat{P}_\xi^2 + \hat{P}_\eta^2 + \hat{P}_\zeta^2 + Q_\xi^{'2} + Q_\eta^{'2} + Q_\zeta^{'2}) \qquad \text{(S.34)}$$

(93 cm^{-1} for $[Fe(CN)_6]^{3-}$ [21]); $\hat{P}_i$ and Q_i are dimensionless operators related to the observables for momentum and position and given by eq.S.35. The vibronic eigenfunctions Ψ of the total

$$\hat{P}_i = \frac{1}{\sqrt{\mu\hbar\omega}}\hat{p}_i; Q_i^{'} = \sqrt{\frac{\mu\omega}{\hbar}}Q_i; i = \xi,\eta,\zeta \qquad \text{(S.35)}$$

Hamiltonian $\hat{H} + \hat{H}_{vib}$ are expressed as a linear combination of products of the spin-orbital basis functions φ_i of $\hat{H}$ and the eigenstates of the states of $\hat{H}_{vib}$ (the three-dimensional harmonic oscillator functions $\chi_j(Q_\xi^{'})\chi_k(Q_\eta^{'})\chi_l(Q_\zeta^{'})$) up to the level n_v:

$$\Psi = \sum_{i=1}^{6}\sum_j\sum_k\sum_l\sum_{j+k+l=0}^{n_v} c_{ijkl}\varphi_i\chi_j(Q_\xi^{'})\chi_k(Q_\eta^{'})\chi_l(Q_\zeta^{'}) \qquad \text{(S.36)}$$

The total basis size N_v without exploitation of the vibronic symmetries is given by eq.S.37,

$$N_v = n_M 6[\frac{n_v(n_v^2 + 6n_v + 11)}{6} + 1] \qquad \text{(S.37)}$$

where n_M is the spin-degeneracy of Cu^{II} (n_M=2) or Ni^{II} (n_M=3). For the moderate vibronic coupling strength obtained in $[Fe(CN)_6]^{3-}$ good accuracy (equal or better than 2%) for the calculated lowest 4 or 6 spin states for Fe^{III}-Cu^{II} and Fe^{III}-Ni^{II}, respectively, and for the **g**-tensor has been achieved with n_v=6, leading to a total dimension of the vibronic matrix of 1008x1008 and 1512x1512, respectively.

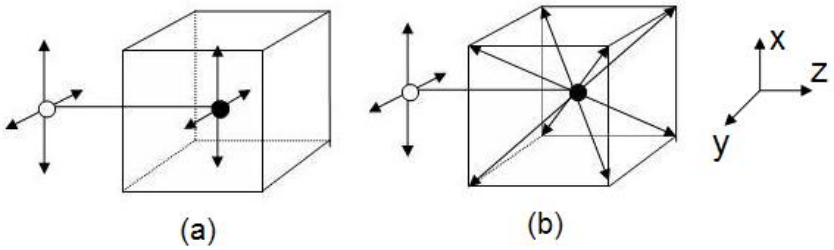

Fig.S.3. (a) The Fe^{III}-M^{II} (M^{II}=Cu^{II},Ni^{II}: white, Fe^{III}: black) pair with a linear Fe^{III}-CN-M^{II} (C_{4v}) bridge and a regular $[Fe(CN)_6]^{3-}$ center; the arrows indicate the directions for optimal π-overlap between the singly occupied t_{2g} ($d_{xz,yz}$) orbitals of Fe^{III} (t_{2g}^5) and the fully occupied d_{xz},d_{yz} orbitals of Cu^{II} (Ni^{II}). (b) The Fe^{III}-M^{II} (M^{II}=Cu^{II},Ni^{II}) pair with a trigonally distorted $[Fe(CN)_6]^{3-}$ center and a $^2A_{1g}$ (d_{z2}, D_{3d}) ground state with d_{z2} lobes pointing towards the body diagonals of a cube with four different (but equivalent) geometries (minima of the ground state potential energy surface, misalignment of the singly occupied d_{z2} orbital of $[Fe(CN)_6]^{3-}$ and the π (d_{xz},d_{yz}) orbitals of Cu^{II} (Ni^{II})).

Effect of the DFT functional on the exchange parameters $J(B_2)[Fe^{III}(e_g^4b_{2g}^1)\text{-}Cu^{II}]$ and $J(E)$ $[Fe^{III}(e_g^3b_{2g}^2\text{-}Cu^{II}]$ and further on the spin-levels and the magnetic anisotropy on Fe^{III}-CN-Cu^{II} exchange pairs without (C_{4v}) and with (C_s) Jahn-Teller distortions of τ_{2g} type.

Table S.1. The exchange coupling energy (J, in cm^{-1}, $H_{exc}=-J\mathbf{S_1S_2}$) for the exchange pair Fe^{III}-CN-$Cu^{II}(d_{z2})$ from DFT broken spin DFT calculations with (SP) and without (SUP) spin-projection, in dependence of the adopted functional and the electronic configuration of Fe^{III}, in comparison with the value deduced from magnetic data.

electronic configuration of $[Fe(CN)_6]^{3-}$	J	VWN	PW91	PBE	OPBE	B3LYP 20%HF	B1LYP 25%HF	B3LYP* 15%HF	Exp.
$b_2^1e^4$	J_{SP} [a]	-45.2	-67.7	-69.2	-112.9	-6.4	1.6	-16.2	17.0 [c]
	J_{SUP} [b]	-22.6	-33.9	-34.7	-56.5	-3.2	0.8	-8.1	13.8;3.9 [d]
$b_2^2e^3$	J_{SP} [a]	114.6	95.2	95.2	103.2	27.4	19.4	35.5	20.9 [e]
	J_{SUP} [b]	57.3	47.6	47.6	51.6	13.7	9.7	17.7	5.0 [f]

[a] Calculated with the spin-projected formula: $J_{SP}=(E_{BS}-E_{HS})/(2S_1S_2)$; E_{BS} and E_{HS} are the energies of the ($\uparrow\downarrow$) broken-spin and the ($\uparrow\uparrow$) high-spin Slater determinants.

[b] Calculated with the spin-unprojected formula: $J_{SUP}=(E_{BS}-E_{HS})/(2S_1S_2+S_2)$, $S_2 \leq S_1$;

[c] Reported from a fit to magnetic susceptibility data of the Cu_3Fe_2 SMM with a d_{x2-y2} ground state of Cu [9]; to compare with the calculated numbers (d_{z2} ground state of Cu^{II}), the experimental energy has to be multiplied by $2/\sqrt{3}$ ($Jd_{z2}=2/\sqrt{3}Jd_{x2-y2}$).

[d] Reported for the two distinct Fe^{III}-CN-Cu^{II} exchange coupled pairs in the $Fe^{III}_2Cu^{II}_3$ complex $[\{Cu(rac\text{-}CTH)\}_3\{Fe(CN)_6\}_2].2H_2O$, rac-CTH= rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane from simulations using a Heisenberg Hamiltonian.[19]

[e] Reported from Monte Carlo simulations of the magnetic properties of heterobimetallic chain $\{[Fe^{III}(bpym)(CN)_4]_2\ M^{II}\ (H_2O)_2\}.6H_2O$, bpym=2,2'-bipyrimidine using an isotropic Heisenberg model.[20]

[f] reported from a fit of the isotropic J to magnetic susceptibility data on the bimetallic complex $[\{Fe^{III}(phen)(CN)_4\}_2Cu^{II}(H_2O)_2].4H_2O$.[21]

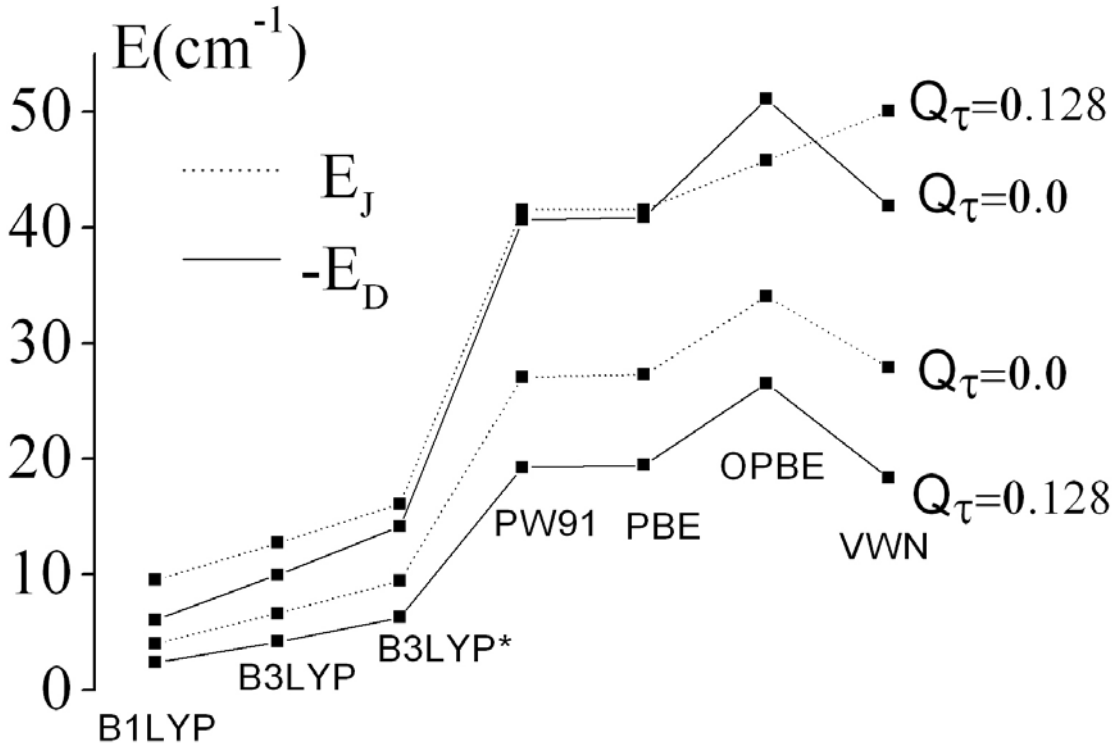

Fig.S.4. Effect of the functional on the E_J and $-E_D$ parameters.

Footnote

[1] Matrix S.12 differs in sign compared to the one given in manuscript reference [22] (and derived in detail the Supporting information there). This is because real spins rather than effective spins of Fe^{III} have been employed in the cited work (implying **g** tensors of Fe^{III} and Cu^{II} which are of the same sign). This has lead to the conventional negative D and a positive J values. Here we should stress, this is only possible if $J(^2B_2)=0$, in which case B_1 and B_2 (Figure 3) become accidentally degenerate. In a consistent description however, one should keep to the definitions and sign conventions of manuscript reference reference [93] which allows also to provide a correct symmetry description.