Supplementary Information for
DFT and TD-DFT studies of electronic structures and one-electron excitation state of cyanide-bridged molecular square complex

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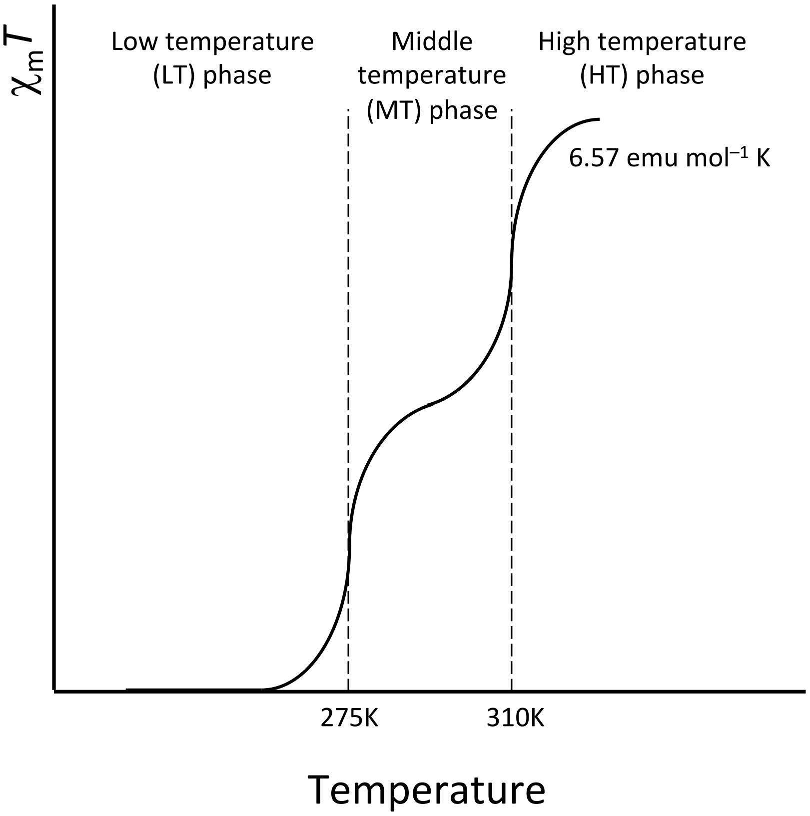

Figure S1. Illustration of experimental $\chi_m T$ vs T plot of $[Co_2Fe_2(CN)_6(tp^*)_2(dtbbpy)_4](PF_6)_2\cdot 2MeOH$ (**1**).

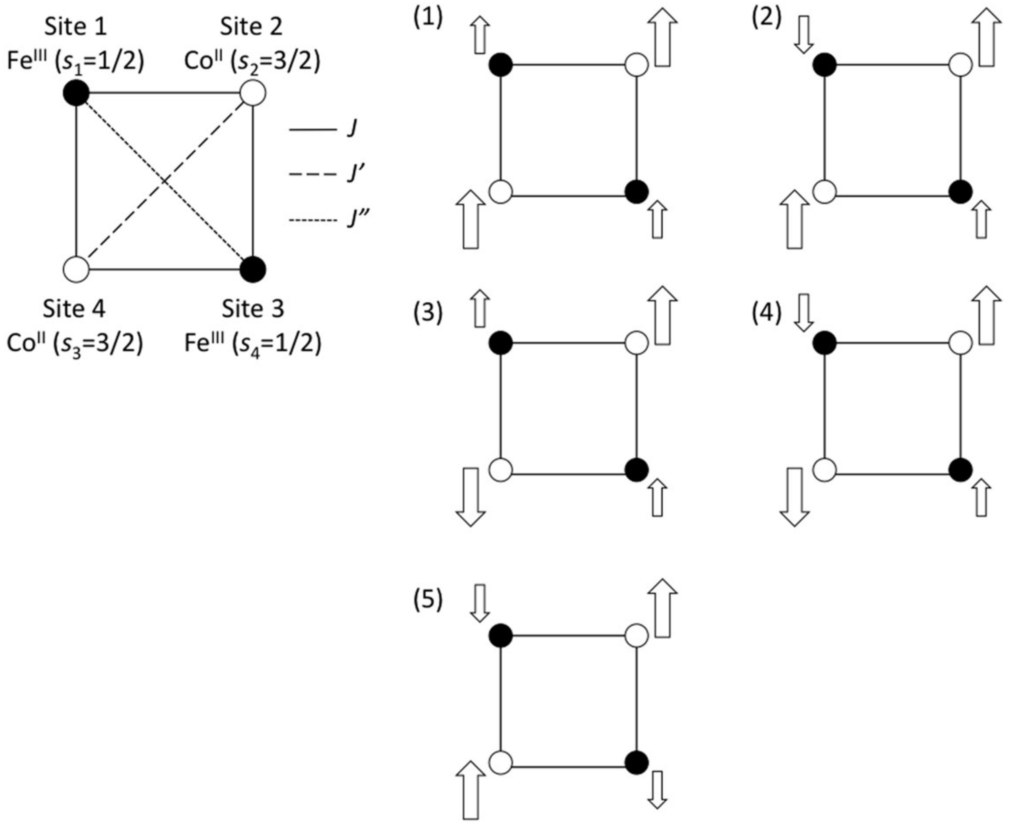

Figure S2. Possible spin-coupling structures in the open-shell [Fe$^{III}_{LS2}$Co$^{II}_{HS2}$] state.

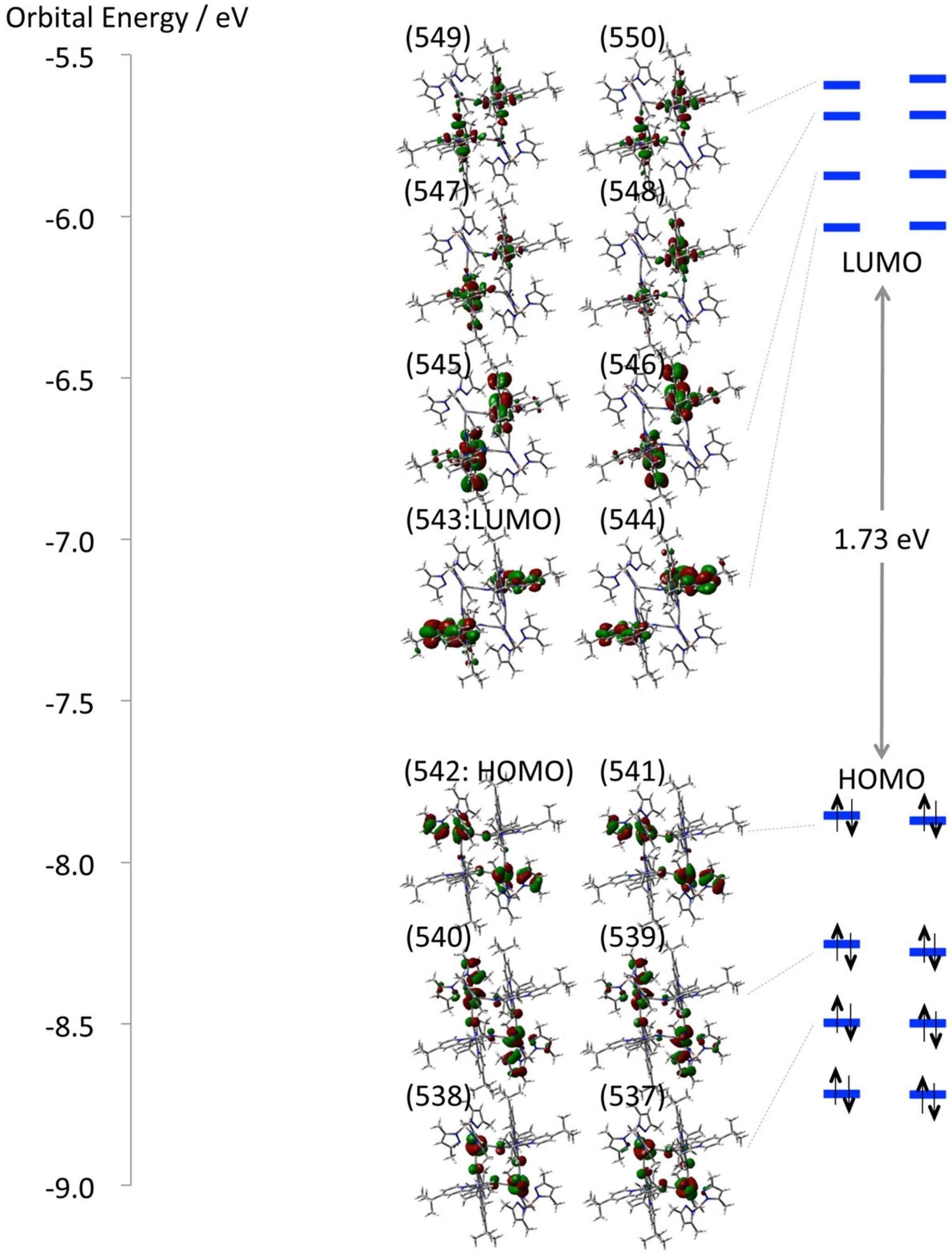

Figure S3 (a) Enlarged picture of Figure 3 (A).

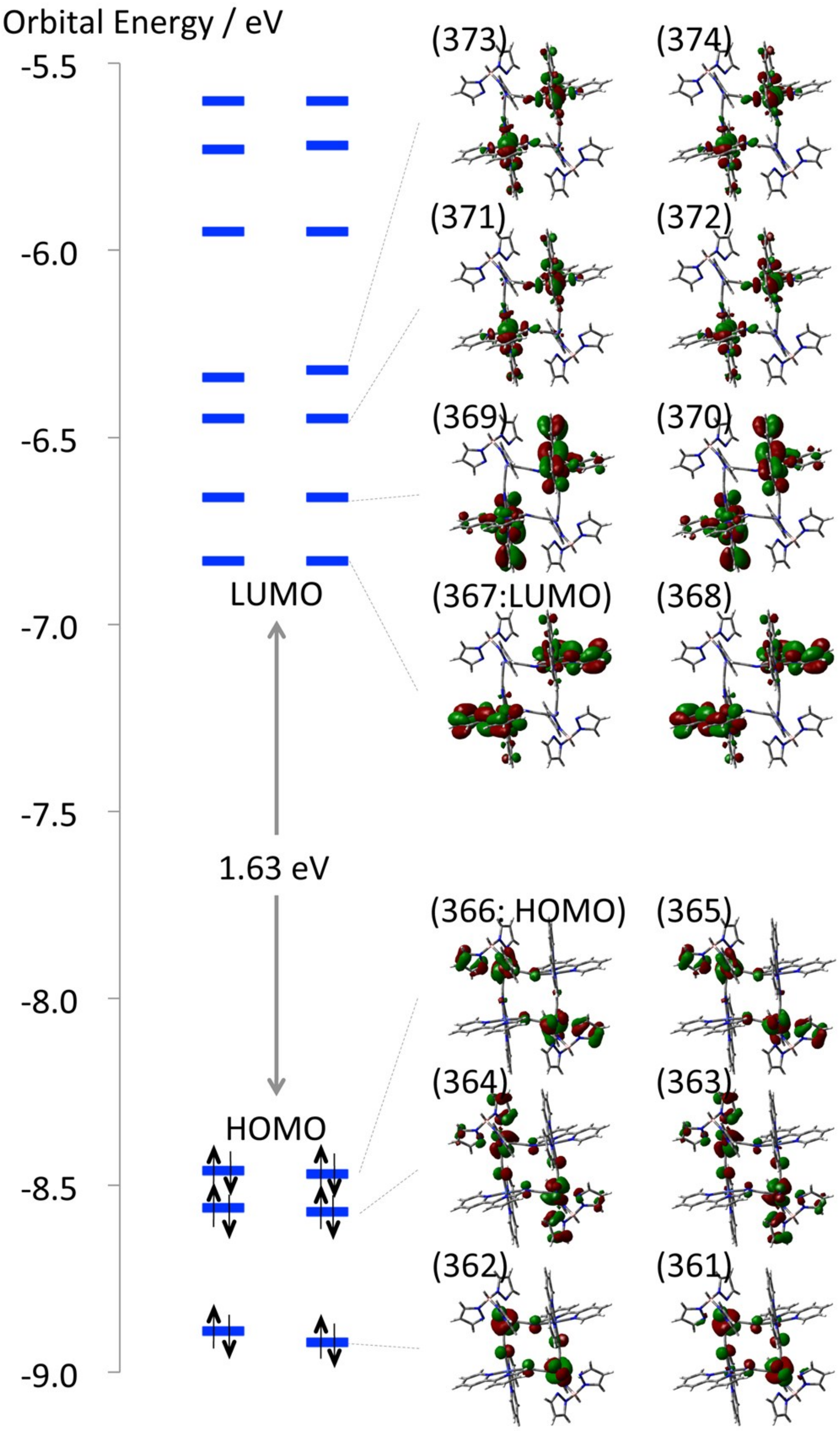

Figure S3 (b) Enlarged picture of Figure 3 (B).

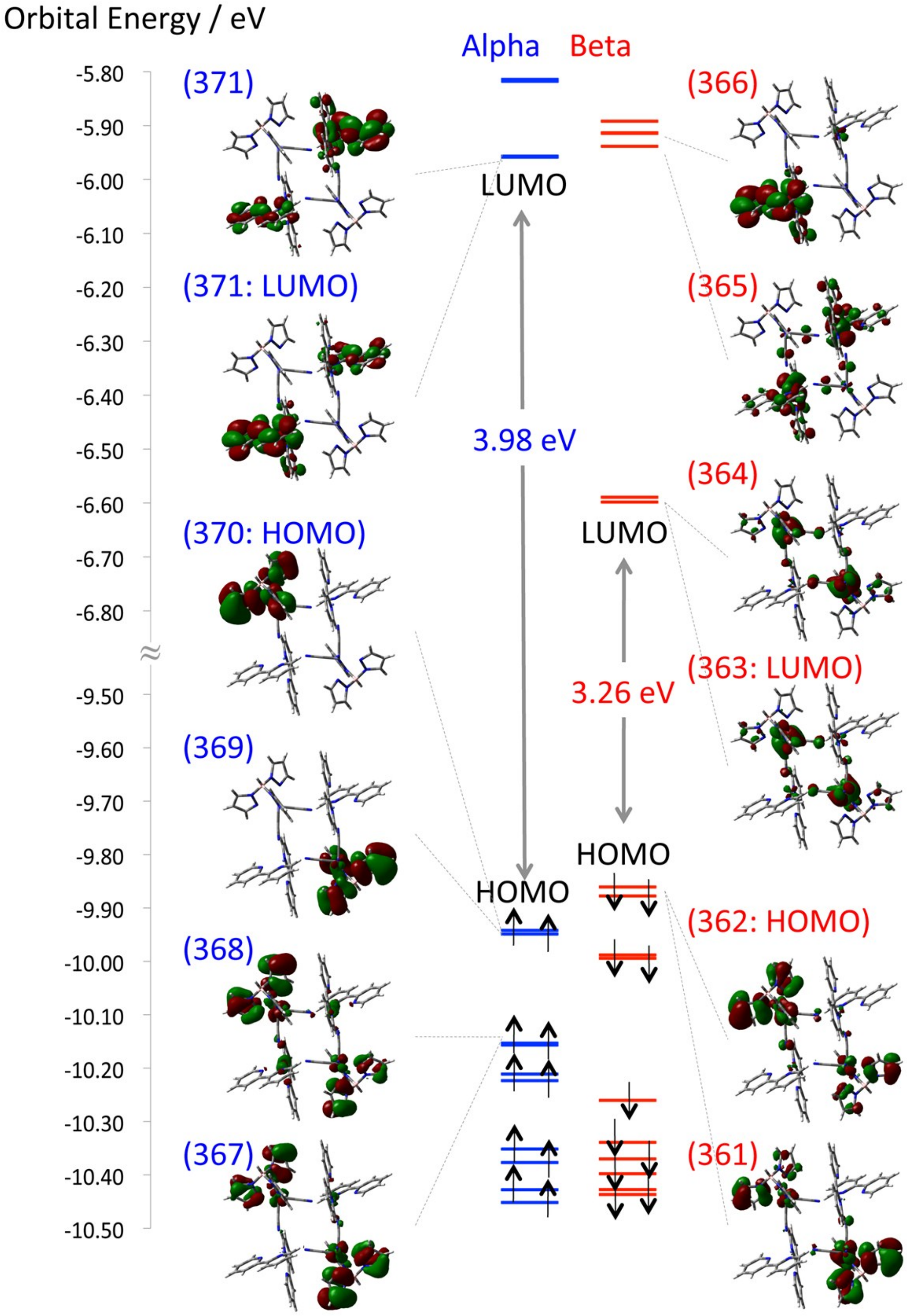

Figure S4 (a) Enlarged picture of Figure 4 (a).

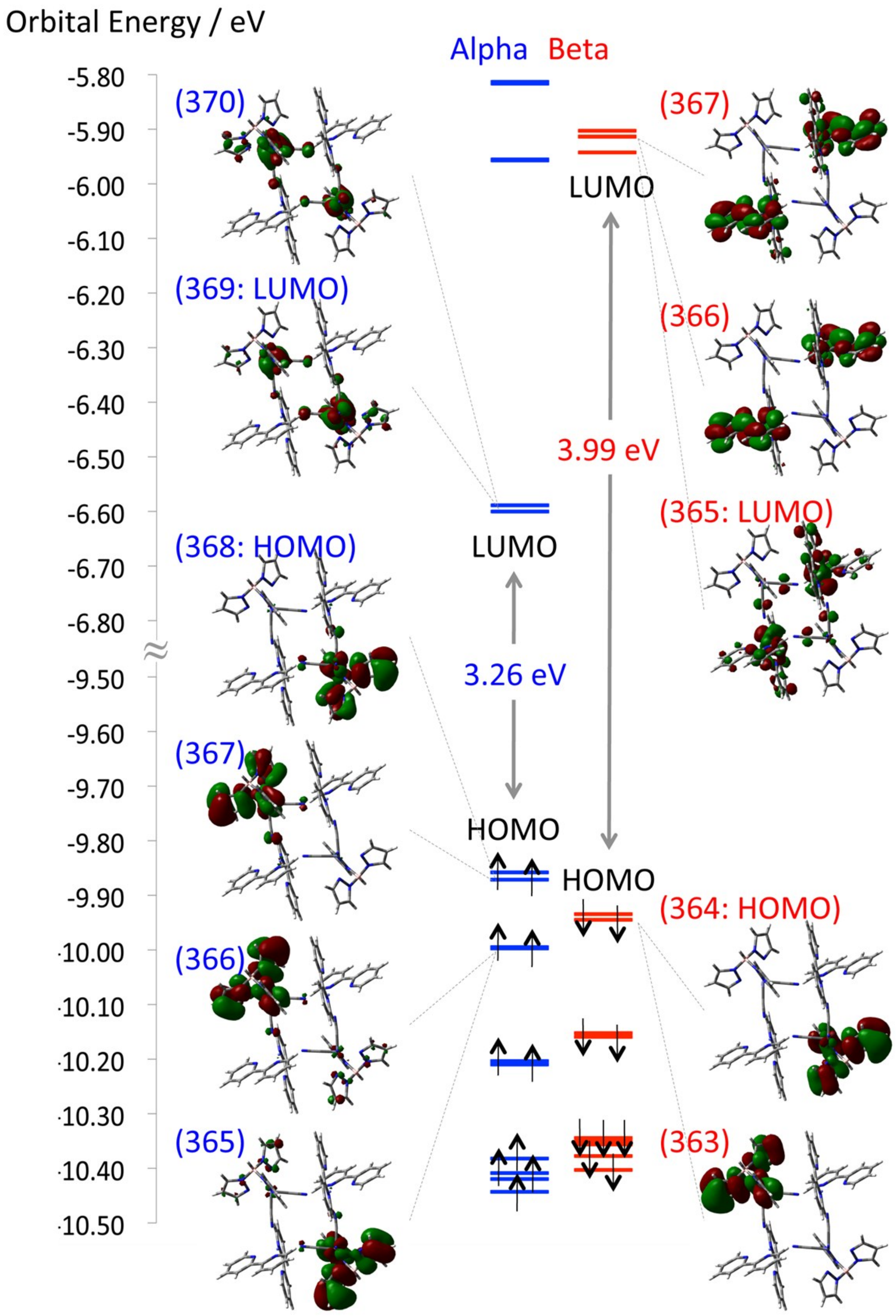

Figure S4 (b) Enlarged picture of Figure 4 (b).

Table S1. Calculated absorption spectra by TD-B3LYP. Absorptions with non-zero oscillator strength are summarized here. ΔE and λ are absorption energies and *f* is a oscillator strengths. Dominant contributions are described by orbital numbers in Figure 3 (b).

state #	ΔE / eV	λ / nm	*f* (a.u.)	Dominant contribution	%
4	1.20	1034	0.0001	365 -> 368	90
5	1.27	976	0.0004	364 -> 367	83
8	1.30	957	0.0015	363 -> 368	78
10	1.32	939	0.0001	365 -> 369 366 -> 370	46 42
11	1.37	908	0.0016	365 -> 370 366 -> 369	60 27
14	1.41	882	0.001	365 -> 371 366 -> 372	43 32
16	1.42	875	0.0001	363 -> 369 364 -> 370	36 46
17	1.44	863	0.0004	363 -> 369 364 -> 370	33 29
19	1.46	850	0.0004	366 -> 372 365 -> 371	37 15
22	1.51	819	0.0035	363 -> 371 364 -> 373	41 25
23	1.52	813	0.0005	366 -> 373 365 -> 371	62 21
25	1.53	810	0.0037	364 -> 372	70
28	1.56	796	0.0012	365 -> 374	80
30	1.59	779	0.0019	362 -> 367	78
31	1.60	776	0.0007	364 -> 373 363 -> 371	32 20
34	1.62	763	0.0015	361 -> 368	83
35	1.63	758	0.0011	363 -> 374 364 -> 373	59 31
38	1.74	711	0.0006	362 -> 370	74
39	1.75	707	0.0004	361 -> 369 361 -> 371	59 17

Derivation of the formula to deduce the J value

The magnetic properties of the polynuclear metal complexes are often discussed using Heisenberg Hamiltonian

$$H = -2\sum J_{\mathrm{ij}} \hat{\boldsymbol{S}}_{\mathrm{i}} \cdot \hat{\boldsymbol{S}}_{\mathrm{j}}, \qquad \text{(S1)}$$

where J_{ij} is the orbital-averaged effective exchange integrals between the spin site i and j with total spin operators $\hat{\boldsymbol{S}}_{\mathrm{i}}$ and $\hat{\boldsymbol{S}}_{\mathrm{j}}$, respectively. As depicted in Figure 2 (a), there are three types interactions i.e. *J*, *J'* and *J"*. However, *J'* and *J"* are considered to be small enough than *J*, so that we consider only the adjacent ones. For simple systems such as linearly aligned two- or multi-spin models, Yamaguchi et al. has proposed that J_{ij} value can be calculated from the energy splitting between a broken-symmetry (BS) anti-ferromagnetic (AF) and a ferromagnetic (F) states by using an equation,

$$J_{\mathrm{ij}} = \frac{{}^{AF}E - {}^{F}E}{\left\langle S^2 \right\rangle^{F} - \left\langle S^2 \right\rangle^{AF}}, \qquad \text{(S2)}$$

where and denote the total energy and total spin angular momentum for the spin state X (X = AF and F), respectively. However, equation (2) cannot apply to the cyclic and plural *J* systems. For such complicated systems, Shoji et al. proposed a general algorithm for calculations of *J* values [M. Shoji, K. Koizumi, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, K. Yamaguchi, Chem. Phys Lett., 432, 343-347, 2006]. The $\left\langle \hat{\boldsymbol{S}}^2 \right\rangle$ value of the BS calculation can be evaluated with a spin correlation function $\left\langle \hat{\boldsymbol{s}}_i \cdot \hat{\boldsymbol{s}}_j \right\rangle$ between spin site *i* and *j*,

$${}^{\mathrm{BS}}\left\langle \hat{\boldsymbol{S}}^2 \right\rangle = \sum_{i=1}^{N} \hat{\boldsymbol{s}}_i \left(\hat{\boldsymbol{s}}_i + 1 \right) + 2\sum_{i<j} \left\langle \hat{\boldsymbol{s}}_i \cdot \hat{\boldsymbol{s}}_j \right\rangle + SP, \qquad \text{(S3)}$$

where $\hat{\boldsymbol{s}}_i$ is a spin operator for the spin site *i* and SP means effect of a spin polarization. If a coupling between sites $\boldsymbol{s}_i$ and $\boldsymbol{s}_j$ is ferromagnetic, the spin correlation function is obtained by

$${}^{\mathrm{F}}\left\langle \hat{\boldsymbol{s}}_i \cdot \hat{\boldsymbol{s}}_j \right\rangle = \left| \hat{\boldsymbol{s}}_i \right| \cdot \left| \hat{\boldsymbol{s}}_j \right|. \qquad \text{(S4)}$$

While a correlation function for anti-ferromagnetic coupling becomes

$${}^{\mathrm{AF}}\left\langle \hat{\boldsymbol{s}}_i \cdot \hat{\boldsymbol{s}}_j \right\rangle = -\left| \hat{\boldsymbol{s}}_i \right| \cdot \left| \hat{\boldsymbol{s}}_j \right| - \frac{N_\beta}{2} T^2, \qquad \text{(S5)}$$

where N_{b} and *T* are a number of beta electrons and overlap between spin orbitals.

Because ${}^{\mathrm{F}}\langle\hat{\boldsymbol{S}}^2\rangle$ and ${}^{\mathrm{AF}}\langle\hat{\boldsymbol{S}}^2\rangle$ are expressed by

$$ {}^{\mathrm{F}}\langle\hat{\boldsymbol{S}}^2\rangle = 20 + SP, \qquad \text{(S6a)} $$

and

$$ {}^{\mathrm{AF}}\langle\hat{\boldsymbol{S}}^2\rangle = 8 + {}^{\mathrm{AF}}\langle\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j\rangle + SP. \qquad \text{(S6b)} $$

Then, ${}^{\mathrm{AF}}\langle\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j\rangle$ is deduced by subtracting ${}^{\mathrm{AF}}\langle\hat{\boldsymbol{S}}^2\rangle$ from ${}^{\mathrm{F}}\langle\hat{\boldsymbol{S}}^2\rangle$ as follows,

$$ {}^{\mathrm{F}}\langle\hat{\boldsymbol{S}}^2\rangle - {}^{\mathrm{AF}}\langle\hat{\boldsymbol{S}}^2\rangle = 6 - 8\,{}^{\mathrm{AF}}\langle\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j\rangle \qquad \text{(S7)} $$

On the other hand, total energies are expressed as

$$ {}^{\mathrm{F}}E = -8J\,{}^{\mathrm{F}}\langle\hat{\boldsymbol{s}}_1\cdot\hat{\boldsymbol{s}}_2\rangle, \qquad \text{(S8a)} $$

$$ {}^{\mathrm{F}}E = -8J\,{}^{\mathrm{AF}}\langle\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j\rangle. $$

(8b)

Then J value between Fe$^{\mathrm{III}}$ and Co$^{\mathrm{II}}$ is obtained from

$$ J = \frac{{}^{\mathrm{AF}}E - {}^{\mathrm{F}}E}{8\left({}^{\mathrm{F}}\langle\hat{\boldsymbol{s}}_1\cdot\hat{\boldsymbol{s}}_2\rangle - {}^{\mathrm{AF}}\langle\hat{\boldsymbol{s}}_1\cdot\hat{\boldsymbol{s}}_2\rangle\right)}. \qquad \text{(S9)} $$

By using the algorithm, *J* value of this cyclic system can be solved by using the formula.

On the other hand, Ising Hamiltonian, which consider only S_{z} component is also often used for a consideration of the magnetic interaction between fully localized spins.

$$ \boldsymbol{H}_{\mathrm{Ising}} = -2\sum J^z_{\mathrm{ij}}\hat{\boldsymbol{S}}^z_i\cdot\hat{\boldsymbol{S}}^z_i \qquad \text{(S10)} $$

spin correlation function of anti-ferromagnetic coupling becomes ${}^{\mathrm{AF}}\langle\hat{\boldsymbol{s}}_i\cdot\hat{\boldsymbol{s}}_j\rangle = -|\hat{\boldsymbol{s}}_i|\cdot|\hat{\boldsymbol{s}}_j|$ which corresponds to fully localized spins on equation 5. Then, from equation 9, *J* becomes

$$ J^z = \frac{{}^{\mathrm{AF}}E - {}^{\mathrm{F}}E}{16|\hat{\boldsymbol{s}}_1|\cdot|\hat{\boldsymbol{s}}_2|} \qquad \text{(S11)} $$

Table S2. Calculated J values, ${}^{\mathrm{AF}}\left\langle \hat{\boldsymbol{s}}_i \cdot \hat{\boldsymbol{s}}_j \right\rangle$ and spin polarization (SP) values with Heisenberg and Ising spin models.

Spin model	${}^{\mathrm{AF}}\left\langle \hat{\boldsymbol{s}}_i \cdot \hat{\boldsymbol{s}}_j \right\rangle$	SP 1)	J values		
			1-L	**1-M**	**1-H**
Heisengerg	–0.750525	0.0485	22	53	11
Ising	–0.750		22	53	11

1) Effect of spin polarization.

Table S3. Calculated relative energies of five spin-coupling states calculated with the **1-H** structure.

State	Site 1 (Fe^{III})	Site 2 (Co^{II})	Site 3 (Fe^{III})	Site 4 (Co^{II})	Sz	Energy / cm^{-1}
	$s_1=1/2$	$s_2=3/2$	$s_3=1/2$	$s_4=3/2$		
1 (**F**)	1	1	1	1	4	-64.2
2	-1	1	1	1	3	0.0
3	1	1	1	-1	1	0.0
4	-1	1	1	-1	0	0.0
5 (**AF**)	-1	1	-1	1	2	64.2

a) 1 and -1 means up and down spins, respectively.