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Density functional study on spin-crossover coordination polymers at a molecular level

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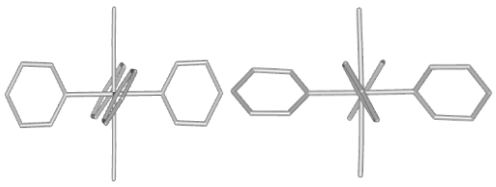
1. INTRODUCTION

Spin-crossover (SCO) behaviors of Fe(II) octahedral complexes can be described as the change of ground-state between low spin (t_{2g}^6) and high spin ($t_{2g}^4e_g^2$). The polymerization of Fe-clusters by bridging ligands has played an important role on controlling whether a SCO phenomenon occurs or not. Coordination polymers (CPs) $[Fe(NCS)_2(L)_2]_n$ (L = 4,4'-azopyridine (azpy)[1)], 1,2-bis(4-pyridyl)ethane (bpa)[2], *N*[1], *N*[2]- bis (pyridine-4-ylmethylene)-ethane-1,2-diamine (bpad)[3)]) have shown the switchable properties of SCO-on/off system in a thermal process. Things to be emphasized among them were the systematic difference in Fe-pyridine dihedral angles between SCO-on and SCO-off (**Figure**). In the present study, we performed a density functional calculation to reveal the spin transition mechanism of SCO-CPs.



SCO-off **SCO-on**

Figure. The structural difference between SCO-on system and SCO-off system.

2. CALCULATION METHOD

All the DFT calculations were performed by using the program "*ORCA*" package. For the purpose of a molecular-level calculation, a mononuclear pyridine model in which bridging ligands were replaced by pyridines, $[Fe(NCS)_2(pyridine)_4]$, was created by cutting out a single-crystal X-ray structure. The structure optimization was performed using a BP86/TZVP method by fixing the dihedral angles. All single point calculations were obtained by a TPSSh/TZVP method, which can reproduce the energy difference among different spin-states in the experiments[4)].

3. RESULTS AND DISCUSSION

All-energy difference between high spin and low spin, $\Delta E_0^{HL} = E_0^{HS} - E_0^{LS}$, including all-electron energy and zero-point energy was shown in **Table**. The sign of ΔE_0^{HL} was reversed depending on whether SCO occurs or not, i.e., the experimental results could be reproduced by our calculation. We will discuss the correlation between a ligand field theory and MOs depending on SCO-on/off.

Table. ΔE_0^{HL} and SCO-on/off (kcal/mol).

L	guest	ΔE_0^{HL}	SCO
azpy	No guest	**-2.4**	off
azpy	EtOH	**0.7**	on
bpa	No guest	**-1.6**	off
bpa	*p*-Dichlorobenzene	**1.2**	on
bpad	MeOH + CH_2Cl_2	**-2.6**	off
bpad	No guest	**0.8**	on

4. REFERENCES

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