**Light and Thermal Induced Spin Crossover Properties of Fe(II) Compound**

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**Abstract.** We synthesized a novel phenanthroline-based mononuclear Fe(II) compound [Fe(TTD)₂(NCS)₂]∙CH₃CN (1, TTD = 1,4,8,9-tetraaza-triphenylene-2,3-dicarbonitrile). And its crystal structure, optical and magnetic properties were analyzed. The thermally induced SCO of the compound is a one-step abrupt transition. In addition, light can also control the spin state of the compound. By using 660 nm light-excited compound, LIESST (light-induced excited spin-state trapping) effect can be achieved.

1. Introduction
Spin crossover (SCO) means the switchability between the high-spin (HS) and low-spin (LS) states of transition-metal complexes [1]. Type of spin crossover transition can be divided into five types: gradual, abrupt, hysteretic, stepped and incomplete [2-4]. So far, Fe(II) compounds with six N atoms coordinated are often used in SCO research because they have significantly different geometric structures and magnetic properties between the HS and LS states [5]. Compared with the diamagnetic LS state, the paramagnetic HS state generally has greater flexibility and distortion in structure. In addition, in the development of spin crossover materials with stored information, the spin transition that exhibits multiple steps at room temperature and is accompanied by thermal hysteresis is the best choice. There are usually two strategies for synthesizing such compounds: The first is through rigid coordination. The body bridges Fe(II) central metal ions to construct a multi-dimensional (1D, 2D and 3D) polymer framework. When spin transformation occurs, due to structural limitations and other factors, it may exhibit an abrupt spin crossover behavior with hysteresis; the second is a mononuclear spin crossover compound that forms a supramolecular network through intermolecular interaction forces (hydrogen bond, halogen bond, π⋯π interaction, etc.). In most cases, such compounds have a wide magnetic hysteresis. 1,10-phenanthroline and its derivatives have been found to be particularly suitable for Fe(II)-N₆ compounds and produce spin crossover behavior [6]. They are also the most in-depth study of spin crossover systems. Since the first o-phenanthroline compound Fe(phen)₂(NCS)₂ (phen = 1,10-phenanthroline) was reported in 1990, research on this type of compound has continued [7]. Among them, the o-phenanthroline derivative [Fe(dpp)₂(NCS)₂]py (dpp = dipyridophenazine, py = pyridine) shows a greater hysteresis, this is because the expanded aromatic ring in the compound presents a strong intermolecular π⋯π interaction, which enhances the result of the intermolecular synergistic interaction [8]. Subsequently, the light-induced excited spin-state trapping effect (LIESST) was also found in the compound [Fe(phen)₂(NCS)₂]. The structure after 30 K light excitation was tested and it was found that the synergistic effect of light-excited metastable HS structure is stronger than that at room temperature.
The powder compound \([\text{Fe(TTD)}_2(\text{NCS})_2] \cdot \text{H}_2\text{O}\) (TTD = 1,4,8,9-tetraaza-triphenylene-2,3-dicarbonitrile) was reported in 2003, showing a two-step incomplete transformation [9]. In this article, we used the same ligand to synthesize \([\text{Fe(TTD)}_2(\text{NCS})_2] \cdot \text{CH}_3\text{CN} \ (1)\) containing different solvent molecule and obtained single crystal structures. We conducted a detailed study of its crystal structure, optical and magnetic properties. The spin crossover behavior is a one-step abrupt spin transition and transition temperature \(T_{1/2}\) is 164 K. In addition, compound can also realize the transition by light excitation, and the relaxation temperature is \(T_{\text{LIESST}} = 70\) K.

2. Materials and Methods

2.1. Experimental test equipment

All chemicals were purchased from commercial sources without further purification. The C, H, N content of the compound was determined and analyzed by EUROVECTER EA3000 elemental analyzer. The PXRD data was measured on the Bruker D8 Advance diffractometer with Cu-Kα (\(\lambda = 1.54056\) Å) as the incident light and tested at 298 K. Infrared spectroscopy is measured on a Bruker ALPHA FT infrared spectrometer with a wavelength range of 4000-400 cm\(^{-1}\) using the KBr tablet method. Differential scanning calorimetry data was measured on PerkinElmer DSC 8000 using aluminum crucible tablet method. The X-ray single crystal diffraction data was tested on the Rigaku Oxford XtaLAB PRO diffractometer using Mo-Kα (\(\lambda = 0.71073\) Å) rays to test the crystal structure, and the Oxford Cryostream 800 system was used to control the temperature to measure the temperature-variable single crystal structure data. The variable temperature magnetic susceptibility test of the compound is measured on a Quantum Design MPMS XL-7 magnetometer, with an external magnetic field of 5000 Oe, the temperature range is 10-300 K, and the temperature change rate is 2 K min\(^{-1}\). In the magnetic test under light conditions, the sample is coated on a transparent tape with a length of about 15 mm \(\times\) 10 mm to make a thin film and loaded into the sample tube. The light beam emitted by the laser is guided to the Quantum Design MPMS XL-7 magnetic field through an optical fiber. The intensity meter cavity is directly irradiated onto the film sample. The light excitation experiment was carried out under the condition of 10 K. When the excitation reached saturation, the light source was turned off, the temperature was raised at 2 K min\(^{-1}\) and the magnetic susceptibility change data was recorded.

2.2 Synthesis of \([\text{Fe(TTD)}_2(\text{NCS})_2] \cdot \text{CH}_3\text{CN}\)

Dissolve Fe(ClO\(_4\))\(_2\) (25.45 mg, 0.1 mmol) and 5 mg of ascorbic acid in 3 mL methanol, mix this solution with 3 mL KSCN (19.43 mg, 0.2 mmol) methanol solution, stir at room temperature for 5 min, filter to obtain a colorless transparent solution. The filtrate was mixed with 6 mL of TTD (56.41 mg, 0.2 mmol) mixed solution (CH\(_2\)Cl\(_2\) / MeOH = 2:1) and stirred, reacted for 5 min and filtered to obtain a dark red precipitate. The dark red precipitate was dissolved in 6 mL of acetonitrile solution, and the dark red block crystals were obtained after being diffused with ether for one week. The yield is about 62\% (calculated based on Fe(ClO\(_4\))\(_2\)). Theoretical element analysis values (%) of the chemical formula C\(_{36}\)H\(_{15}\)FeN\(_{15}\)S\(_2\) (Mr = 777.58): C 55.60, H 1.94, N 27.02; Experimental values: C 55.77, H 1.86, N 27.11. FT-IR (KBr, cm\(^{-1}\))): 734, 817, 1078, 1140, 1216, 1272, 1375, 1398, 1448, 1510, 1573, 2359, 3079.

Fig. 1. Infrared spectrum of compound 1.
3. Results & Discussion

3.1. Crystal structure analysis
Single crystal X-ray data analysis shows that compound 1 is crystallized in the $P2_1/c$ space group, and its smallest asymmetric unit contains a neutral molecule [Fe(TTD)$_2$(NCS)$_2$] and a free acetonitrile solvent molecule, such as Fig. 2. The four N atoms of the two TTD ligands and the two N atoms of the two NCS anions chelate and coordinate with the metal center Fe(II), forming a pseudo-octahedral geometry of Fe(II)-N$_6$.

![Fig. 2. The asymmetric unit of compound 1 (orange Fe; blue N; gray C; yellow S).](image)

Compound 1 has an average Fe-N bond length of 1.971 Å at 120 K, and Fe(II) is in a low-spin state; when the temperature rises to 293 K, the average Fe-N bond length increases to 2.169 Å, it shows that the Fe(II) is high-spin. The high and low temperature Fe-N bond length of compound 1 has changed by 0.198 Å, which is consistent with the change of the average Fe-N bond length (about 0.20 Å) when the compound undergoes spin transition [10], indicating that the metal central ion Fe(II) of compound 1 changes from a high-spin state to a low-spin state as the temperature decreases.

| Temperature | 120 K  | 293 K |
|-------------|--------|-------|
| Fe1-N1 / Å  | 1.974(2) | 2.186(0) |
| Fe1-N2 / Å  | 2.001(0) | 2.225(2) |
| Fe1-N3 / Å  | 1.978(2) | 2.184(7) |
| Fe1-N4 / Å  | 1.980(5) | 2.273(3) |
| Fe1-N5 / Å  | 1.947(2) | 2.070(2) |
| Fe1-N6 / Å  | 1.950(0) | 2.077(2) |
| Fe-N$_{Ave}$ / Å | 1.971(8) | 2.169(4) |
Fig. 3. The crystal packing diagram of compound 1 on the bc plane.

Fig. 4. The interaction between π‧‧‧π and S‧‧‧π of compound 1 (a), C–H‧‧‧S force (b).

The different interactions between molecules often exhibit different spin crossover behaviors. Therefore, analyzing the changes in the intermolecular interactions before and after the compound conversion is more helpful to understand the spin crossover behavior. Analyzing the molecular stacking structure of compound 1 found that because TTD ligand and NCS⁻ are rich in N sources, the intermolecular N‧‧‧H hydrogen bonding force is widely present between molecules. As shown in Fig. 3, intermolecular hydrogen bonds on the bc plane of compound 1 connect the zero-dimensionally dispersed compound 1 to form a two-dimensional supramolecular grid structure. The hydrogen bond is mainly composed of the CN group of the TTD ligand and the hydrogen atom on the adjacent TTD ligand. At the same time, the intermolecular hydrogen bond force gradually increases with the decrease of temperature (Table 2). This is because cooling will induce the spin state transition of the compound 1 and cause the crystal unit cell volume to decrease. The strongest N‧‧‧H hydrogen bond force in the compound is 2.214(6) Å (293 K). As the temperature decreases to 120 K, the hydrogen bond force increases to 2.172(9) Å. The existence of these hydrogen bonding forces effectively enhances the synergistic interaction between the compound molecules, resulting in the magnetic properties of compound 1 showing an abrupt spin crossover behavior (see magnetic analysis).

Table 2. Intermolecular interaction of compound 1.

| Temperature | 120 K   | 293 K   |
|-------------|---------|---------|
| C3-H3···N5  | 3.392(2)| 3.371(9)|
| C17-H17···N10| 3.228(1)| 3.349(4)|
| C24-H24···N11| 3.341(2)| 3.409(6)|
3.2. PXRD and DSC analysis
The synthesized fresh sample of compound 1 was directly subjected to PXRD test at room temperature, and the test data results are in good agreement with the single crystal X-ray diffraction simulation pattern, which proves that the sample is pure phase (Fig. 5). In order to further verify the spin crossover properties of compound 1, we performed a DSC test. As shown in Fig. 6, the exothermic and endothermic peaks were detected during the cooling and heating processes. The endothermic peak at 162 K during heating is basically the same as the spin temperature ($T_{1/2} = 164$ K), but there is a difference between the exothermic peak at 151 K and the transition temperature during cooling, which may be due to the deviation of the cooling rate.

![Fig. 5. PXRD data graph of compound 1.](image)

![Fig. 6. DSC curve of compound 1.](image)
3.3. Magnetic properties analysis

Measuring the variable temperature molar magnetic susceptibility of compound is the most direct way to judge whether it has spin crossover behavior. We measured the variable temperature magnetic susceptibility of compound 1 in the range of 10-300 K, as shown in Fig. 7. The molar susceptibility $\chi_M T$ value of compound 1 at 300 K is $3.32 \text{ cm}^3 \text{ K mol}^{-1}$, which is close to the theoretical $\chi_M T$ value of a high-spin Fe(II) (3.0 cm$^3$ K mol$^{-1}$, $S = 2$) [11]. Upon cooling with 2 K min$^{-1}$, the $\chi_M T$ value above 220 K basically remains unchanged. From 220 K to 120 K, the $\chi_M T$ value begins to rapidly decrease to 0.04 cm$^3$ K mol$^{-1}$, and finally stabilizes the temperature drops to 10 K, which indicates that Fe(II) ion has completely transformed into a low-spin state. The heating process of compound 1 is consistent with the cooling process without magnetic hysteresis, which indicates that the thermally induced spin crossover behavior of compound 1 is completely reversible. Therefore, we can conclude that compound 1 has undergone a one-step abrupt spin transformation process, and its transition temperature $T_{1/2}$ is 164 K.

In addition to thermal-induced reversible spin state transition of compound 1, spin state switching can also be achieved by light (Fig. 7). We performed a light-induced excited spin state trapping effect (LIESST) experiment on the compound at 10 K and found that after irradiating the sample with a 660 nm laser, its $\chi_M T$ value began to increase slowly. After being excited for one hour, the $\chi_M T$ value of the compound reached a stable value of $1.40 \text{ cm}^3 \text{ K mol}^{-1}$. After the light source is turned off, the temperature is increased at a rate of 2 K min$^{-1}$. Due to the metastable high-spin Fe(II) zero-field splitting effect, the $\chi_M T$ value begins to rise to the saturation value of $1.68 \text{ cm}^3 \text{ K mol}^{-1}$ with the increase in temperature, indicating that about 49% of the low-spin Fe(II) is excited into a metastable high-spin state. Subsequently, the compound undergoes a thermal relaxation process, and its $\chi_M T$ value gradually decreases, and completely returns to the low spin state before light induction at 80 K, and the relaxation temperature $T_{\text{LIESST}}$ is 70 K.

![Fig. 7. Thermally and light-induced Magnetic susceptibilities of compound 1.](image)

4. Conclusions

We synthesized an example of Fe(II) o-phenanthroline spin crossover compound, and analyzed its crystal structure, optical and magnetic properties. The thermally induced SCO of compound 1 is a one-step abrupt spin transition. In addition, light can also control the spin state of compound 1, and the LIESST effect is achieved by using 660 nm light to excite the compound. As a result, such compounds can be taken into consideration in the design of compound synthesis to promote the research of new optically functional Fe(II) spin crossover compound materials.

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