

# Manipulating the Spin Crossover Behavior in a Series of $\{\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\}$

## Complexes

Jia-Tao Chen,<sup>#</sup> Xin-Hua Zhao,<sup>#</sup> and Yuan-Zhu Zhang<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, Southern University of Science and Technology, Shenzhen, 518055, China.

### Table of contents

|                               |   |
|-------------------------------|---|
| 1. X-ray crystallography..... | 2 |
| 2. Thermal analysis.....      | 6 |
| 3. Infrared spectra.....      | 7 |

# 1. X-ray crystallography

**Table S1.** Selected bond lengths (Å) and bond angles (deg) for compounds **1·S·3·S**.

| Bond Lengths (Å)  |            |            |            |            |            |            |
|-------------------|------------|------------|------------|------------|------------|------------|
| Compound          | 1·S        |            | 2·S        |            | 3·S        |            |
| Temperature / K   | 100        | 300        | 100        | 300        | 100        | 300        |
| Fe(1)-N(1)        | 1.978(2)   | 1.982(2)   | 1.979(4)   | 1.987(3)   | 1.994(3)   | 2.071(3)   |
| Fe(1)-N(2)        | 2.034(2)   | 2.034(2)   | 2.040(4)   | 2.053(4)   | 2.055(4)   | 2.141(3)   |
| Fe(1)-N(3)        | 1.906(2)   | 1.909(2)   | 1.920(4)   | 1.936(4)   | 1.932(4)   | 1.996(3)   |
| Fe(2)-N(7)        | 1.979(2)   | 1.984(3)   | 2.001(4)   | 2.032(4)   | 1.985(4)   | 2.007(3)   |
| Fe(2)-N(9)        | 1.958(2)   | 1.965(2)   | 2.005(5)   | 2.012(4)   | 2.002(4)   | 2.003(3)   |
| Fe(2)-N(11)       | 1.983(2)   | 1.975(3)   | 2.022(4)   | 2.006(4)   | 2.004(4)   | 2.029(3)   |
| Fe(2)-C(19)       | 1.902(2)   | 1.899(3)   | 1.906(5)   | 1.920(5)   | 1.911(5)   | 1.941(4)   |
| Fe(2)-C(20)       | 1.927(3)   | 1.920(4)   | 1.921(5)   | 1.918(5)   | 1.932(5)   | 1.926(4)   |
| Fe(2)-C(21)       | 1.913(3)   | 1.921(5)   | 1.913(8)   | 1.916(7)   | 1.932(5)   | 1.934(5)   |
| Bond Angles (°)   |            |            |            |            |            |            |
| Compound          | 1·S        |            | 2·S        |            | 3·S        |            |
| Temperature / K   | 100        | 300        | 100        | 300        | 100        | 300        |
| N(3)-Fe(1)-N(3)#1 | 91.09(11)  | 91.11(14)  | 88.2(2)    | 88.6(2)    | 88.9(2)    | 90.58(17)  |
| N(3)-Fe(1)-N(1)   | 91.70(6)   | 91.85(9)   | 93.06(15)  | 93.10(14)  | 92.94(14)  | 93.00(12)  |
| N(3)#1-Fe(1)-N(1) | 86.52(6)   | 86.81(9)   | 88.84(15)  | 88.92(14)  | 89.41(14)  | 91.12(12)  |
| N(3)#1-Fe(1)-N(2) | 91.19(7)   | 91.04(10)  | 92.52(17)  | 92.37(15)  | 92.87(15)  | 92.87(12)  |
| N(3)-Fe(1)-N(2)   | 173.51(6)  | 173.29(9)  | 174.26(15) | 173.83(14) | 173.44(13) | 171.19(12) |
| N(1)-Fe(1)-N(1)#1 | 177.44(9)  | 178.09(14) | 177.4(2)   | 177.2(2)   | 177.7(2)   | 174.14(18) |
| N(1)-Fe(1)-N(2)#1 | 99.49(6)   | 99.46(9)   | 96.80(17)  | 97.11(15)  | 96.82(14)  | 96.79(12)  |
| N(1)-Fe(1)-N(2)   | 82.38(6)   | 81.93(9)   | 81.27(16)  | 80.83(14)  | 80.76(14)  | 78.84(12)  |
| N(2)-Fe(1)-N(2)#1 | 87.20(9)   | 87.54(14)  | 87.3(3)    | 87.3(2)    | 86.1(2)    | 84.90(17)  |
| C(19)-N(3)-Fe(1)  | 178.19(17) | 178.2(2)   | 174.8(4)   | 175.0(3)   | 175.6(3)   | 175.3(3)   |
| N(3)-C(19)-Fe(2)  | 176.21(18) | 177.3(3)   | 173.2(4)   | 173.2(4)   | 172.1(4)   | 172.3(3)   |

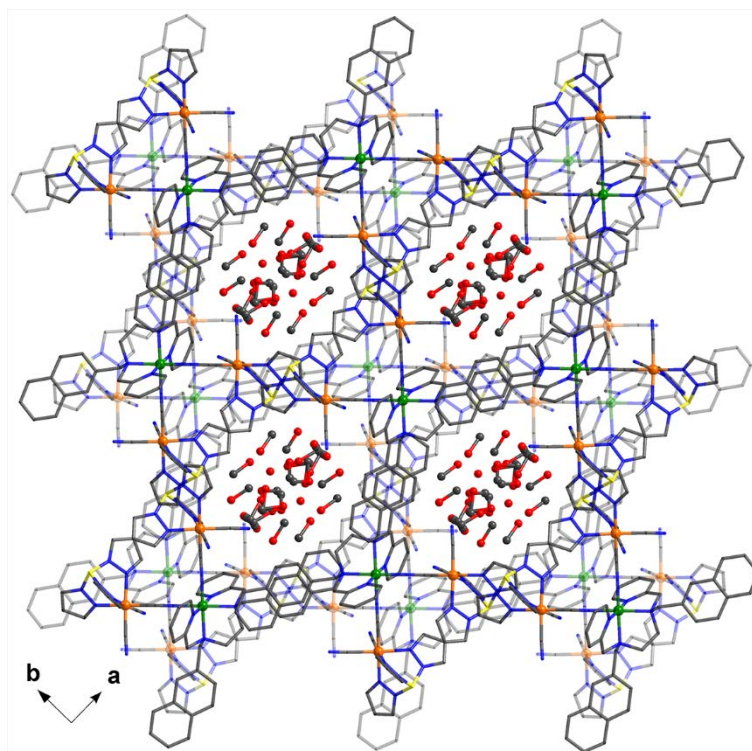
#1 -x+1, y, -z+1/2

**Table S2.** The hydrogen bonds in compound **1·S** at 100 K.

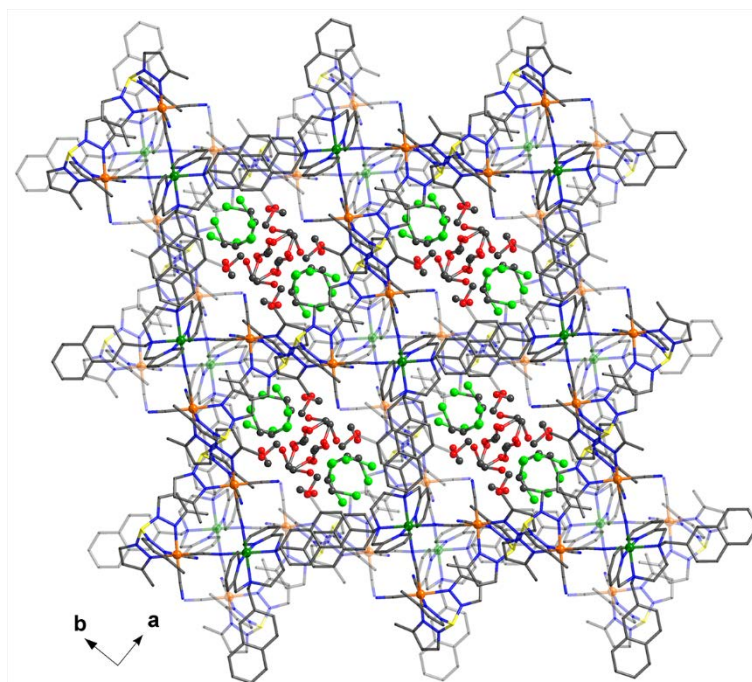
| D-H...A             | D-H (Å) | H...A (Å) | D...A (Å) | ∠D-H...A (deg) |
|---------------------|---------|-----------|-----------|----------------|
| O(2)-H(2A)···N(4)#1 | 0.84    | 1.99      | 2.82(1)   | 169.1          |
| O(3)-H(3A)···O(3A)  | 0.84    | 1.70      | 2.53(2)   | 170.8          |
| O(3)-H(3A)···O(4)   | 0.84    | 2.01      | 2.83(1)   | 168.4          |
| O(3A)-H(3AA)···O(3) | 0.84    | 1.90      | 2.53(2)   | 131.0          |
| O(5)-H(5A)···O(1A)  | 0.87    | 2.09      | 2.75(1)   | 131.9          |
| O(5)-H(5B)···O(3)   | 0.87    | 1.92      | 2.78(1)   | 167.7          |
| #1 = 1-x, +y, 0.5-z |         |           |           |                |

**Table S4.** The hydrogen bonds in compound **3**·S at 100 K.

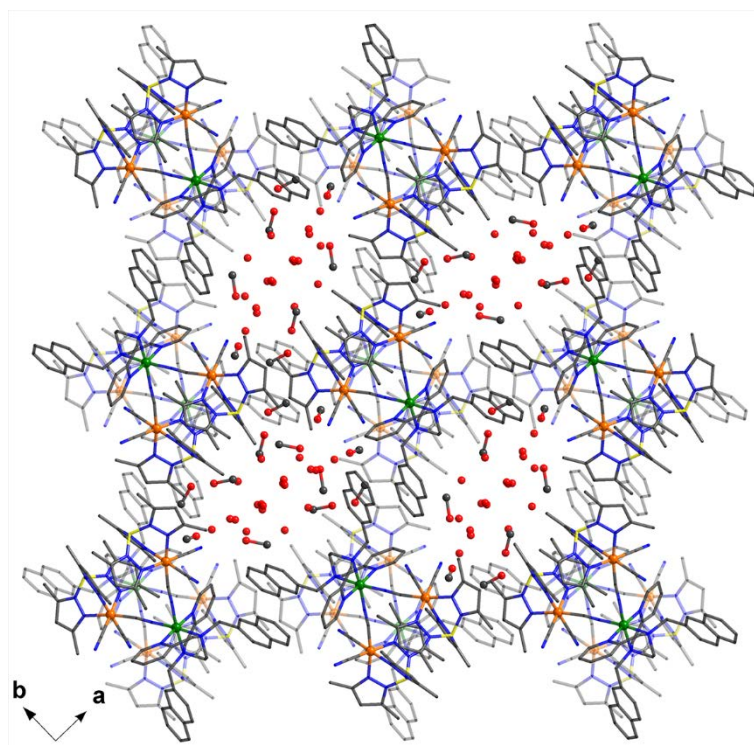
| D-H···A                                                                                                                                                                  | D-H (Å) | H···A (Å) | D···A (Å) | ∠D-H···A (deg) |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------|-----------|-----------|----------------|
| O(6A)-H(6AB) ···N(4)#1                                                                                                                                                   | 0.87    | 2.02      | 2.85(1)   | 158.5          |
| O(4)-H(4A) ···O(7)#2                                                                                                                                                     | 0.87    | 2.03      | 2.60(4)   | 121.7          |
| O(4)-H(4B) ···O(5)#3                                                                                                                                                     | 0.87    | 2.40      | 2.90(3)   | 117.0          |
| O(1)-H(1B) ···N(5)#4                                                                                                                                                     | 0.84    | 2.28      | 2.86(1)   | 126.3          |
| O(5)-H(5A) ···O(1)                                                                                                                                                       | 0.87    | 1.95      | 2.73(2)   | 148.8          |
| O(5)-H(5B) ···O(8)#5                                                                                                                                                     | 0.87    | 1.82      | 2.56(2)   | 141.2          |
| O(2)-H(2A) ···O(6A)                                                                                                                                                      | 0.84    | 1.97      | 2.72(2)   | 147.7          |
| O(7)-H(7B) ···O(4)#2                                                                                                                                                     | 0.87    | 1.82      | 2.60(4)   | 147.8          |
| C(39A)-H(39C) ···O(6A)#6                                                                                                                                                 | 0.98    | 1.79      | 2.65(3)   | 144.3          |
| C(37)-H(37C) ···O(6B)#1                                                                                                                                                  | 0.98    | 1.61      | 2.39(4)   | 133.2          |
| C(39B)-H(39D) ···O(1)#7                                                                                                                                                  | 0.98    | 1.91      | 2.75(4)   | 141.8          |
| #1 = 1-x, +y, 3/2-z; #2 = 1/2-x, 3/2-y, 1-z; #3 = -1/2+x, 1/2+y, +z; #4 = +x, 1-y, -1/2+z;<br>#5 = 3/2-x, -1/2+y, 3/2-z; #6 = 1/2+x, 1/2+y, +z; #7 = 3/2-x, 1/2+y, 3/2-z |         |           |           |                |



**Figure S1.** The crystal packing of **1·S** along *c* axis with lattice solvent molecules in the 1D channels.

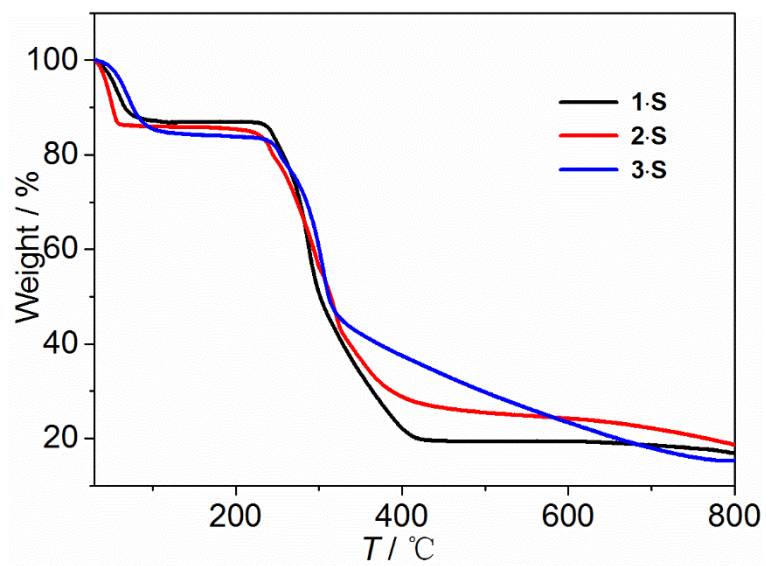


**Figure S2.** The crystal packing of **2·S** along *c* axis with lattice solvent molecules in the 1D channels.



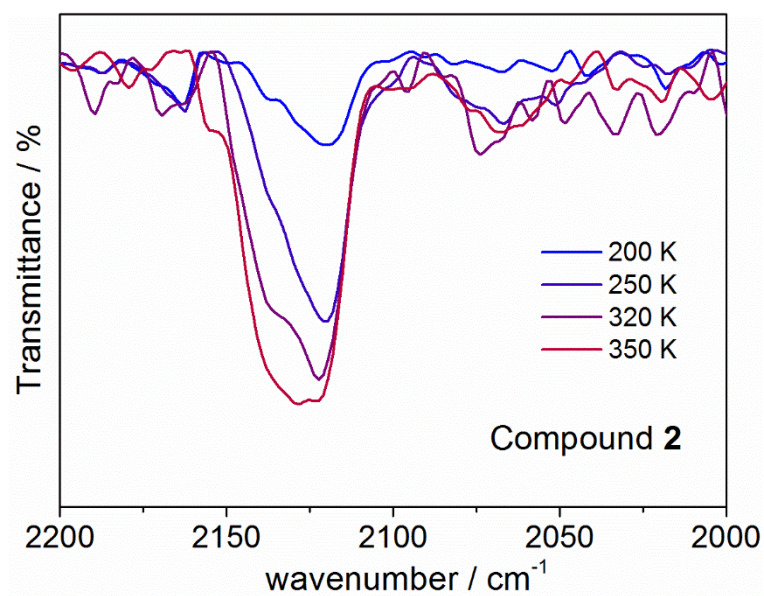
**Figure S3.** The crystal packing of **3·S** along c axis with lattice solvent molecules in the 1D channels.

## 2. Thermal Analysis.

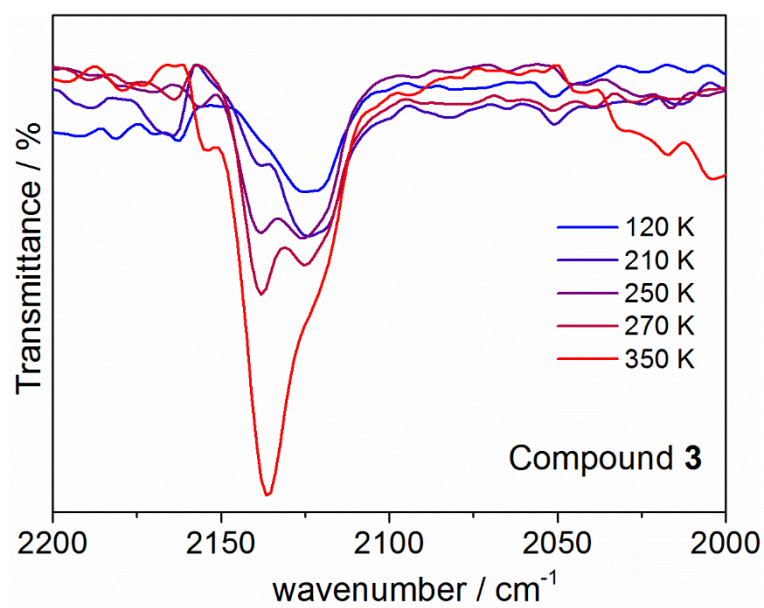


**Figure S4.** TGA curves of compounds **1·S** to **3·S** at a rate of 5 K/min under an argon atmosphere.

### 3. Infrared spectra.



**Figure S5.** The variable temperature infrared spectra of compound 2.



**Figure S6.** The variable temperature infrared spectra of compound 3.