**Supporting Information**

**Heteroleptic and Homoleptic Iron(III) Spin-crossover complexes; effects of ligand substituents and intermolecular interactions between co-cation/anion and the complex.**

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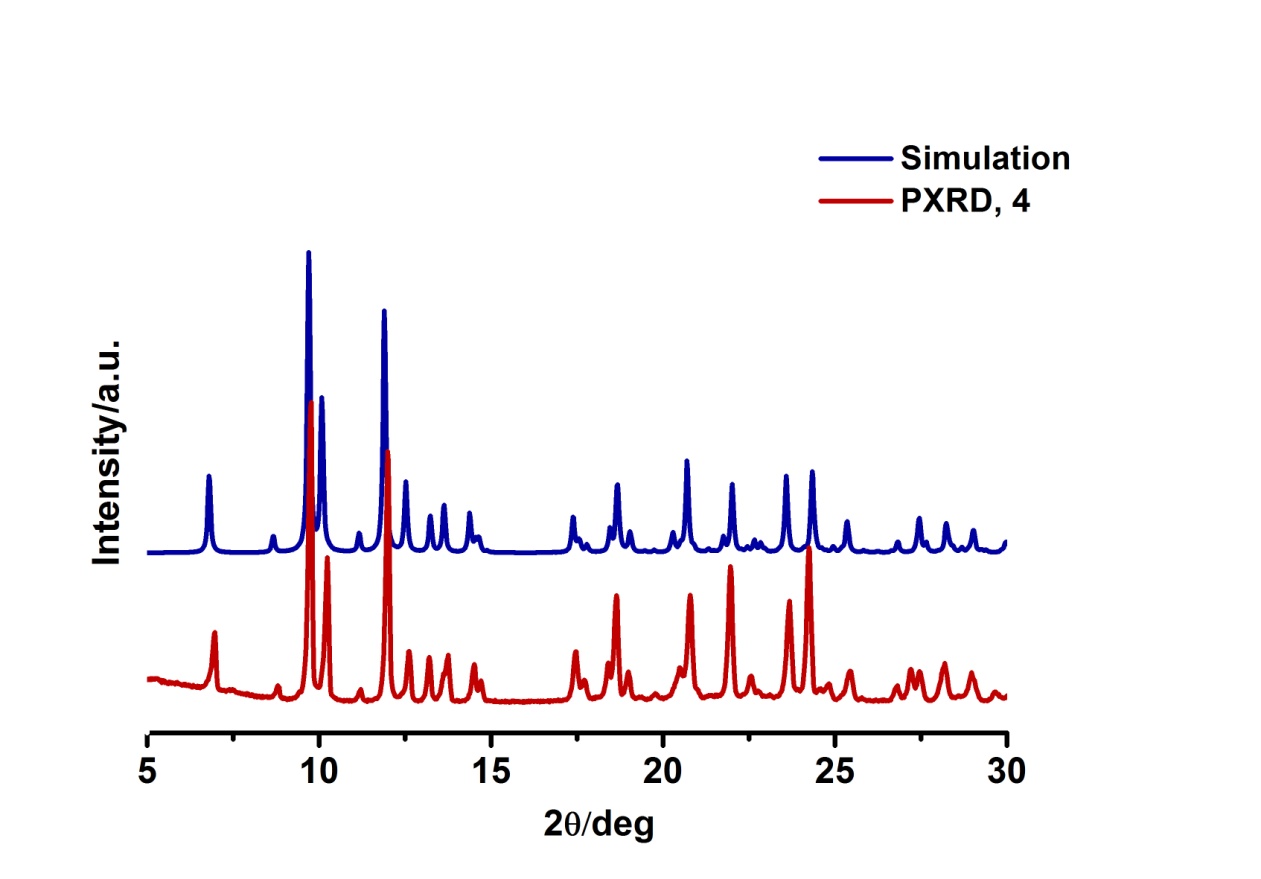
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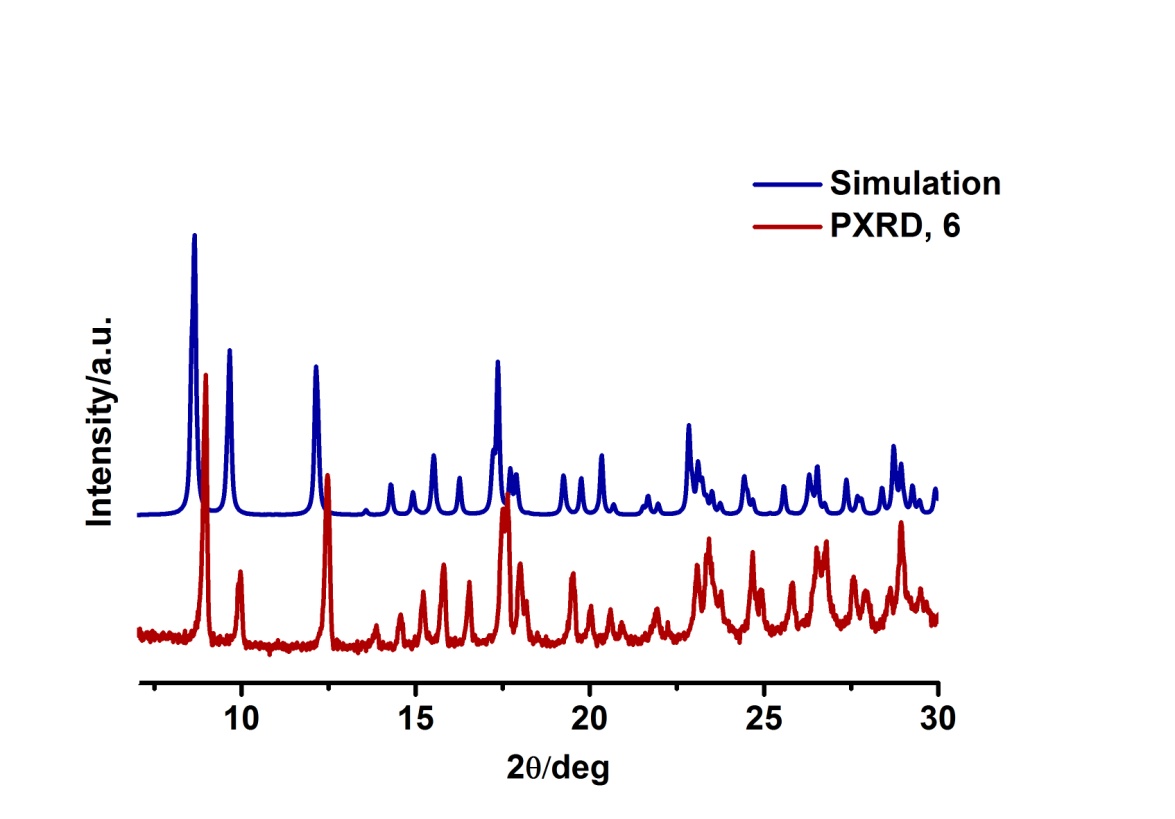
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**Figure S1** Powder Xray diffractograms for **4** and **6(bulk)**.

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| |  |  | | --- | --- | |  |  | |  |  | |

**Figure S2** Variable-temperature magnetic susceptibility (χMT) measurements for **3** – **6(bulk)**

|  |  |
| --- | --- |
|  |  |
| **(a)** | **(b)** |
|  | |
| **(c)** | |

**Figure S3** The asymmetric unit of (a) **1** [1] and (b) **2** and (c) representation of an octahedral environment around Fe(III) of **2**. Color code: orange: iron, red: oxygen, dark blue: nitrogen, yellow: sulphur, grey: carbon and light grey; hydrogen

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|  |

**Figure S4** The angle between planes of each ligand component of **2**

**Table S1** Comparison of the octahedral parameters and the angle of the ligand component planes between **1** and **2**

|  |  |  |
| --- | --- | --- |
| **100 K** | **1** [1] | **2** |
| Σ/° | 44 | 51 |
| Θ/° | 80 | 98 |
| φ/° (thsa) | 13 | 23 |
| ϕ/° (3-MeOSalEen ) | 16 | 19 |

**Table S2** Intermolecular interactions in [Fe(3-MeOSalEen)(3-EtOthsa)] **2**at 100 K; in Å.

|  |  |
| --- | --- |
| Interactions/Å | **100 K** |
| 1D chain along c axis |  |
| C7-H7··· π | 3.051 |
| C23-H23A··· C18 | 2.8541(4) |
| 1D chain along b axis |  |
| C11-H11B···C2 | 2.8731(6) |
| C9-H9B···C5 | 2.6990(7) |
| C9-H9B···C6 | 2.8822(4) |
| C9-H9B···C7 | 2.8900(5) |
| C7-H7···S1 | 2.9341(5) |
| C8-H8A···S1 | 2.8698(4) |
| N4-H4B···O3 | 2.2869(3) |
| N4-H4A···N5 | 2.0996(4) |
| 1D chain along a axis |  |
| C3-H3···C15 | 2.8790(5) |
| C3-H3···C16 | 2.7033(7) |
| C20-H20C···O2 | 1.9890(6) |
| C22-H22A···C4 | 2.8757(11) |

|  |  |
| --- | --- |
| **(a)** |  |
|  | Two types of π-π interaction   * thsa-thsa, 3 Å * 3-MeOSalEen-3-MeOSalEen, 3 Å |
| **(b)** |  |
|  | * thsa-3-MeOSalEen, No π-π interaction, (centroid-centroid 4.7 Å, No π-π interaction) * C-H∙∙∙C/π interactions |

**Figure S5** Comparison of the Fe(III) molecule arrangements in a chain motif of (a) **1** [1]and (b) **2**

|  |  |
| --- | --- |
|  |  |
| a 1D chain   * π-π interaction, 3.69 Å * π-π interaction, 3.0 Å | |
| **(a)** | |
|  |  |
| * No π-π interaction, 4.13 Å * C-H∙∙∙C/π interactions, (centroid-centroid 4.7 Å, No π-π interaction) | |
| **(b)** | |

**Figure S6** Another one dimensional packing comparison between (a) **1** [1] and (b) **2** and (rhs) turning 90 degree stacking view showing the high degree of packing order in **1**

|  |
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|  |

**Figure S7** Representation of **3** (as an example) showing the anion occupation along the c axis with the plane-plane distance about 6 Å. For **4**, the plane-plane distance is about 6.3 Å.

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| --- | --- |
|  |  |

**Figure S8** The superimposition of the Fe(III) molecules of **3** (cyan) and **4** (yellow) in wireframe model

**Table S3** Intermolecular interactions in [Fe(3-EtOSalEen)2]NO3 **3** and [Fe(3-EtOSalEen)2]Cl **4** at 100 K

|  |  |  |
| --- | --- | --- |
| Interactions/Å | **3** | **4** |
| Chain along the a axis |  |  |
| C17-H17∙∙∙O1 | 2.6415(9) | 2.6764(23) |
| C15-H15B∙∙∙C1 | 2.9163(10) | 2.8379(39) |
| C2-H2B∙∙∙π | 2.699 | 2.590 |
| P4AE |  |  |
| π-π | 3.258 | 3.245 |
| C18-H18∙∙∙π | 2.766 | 2.752 |
| along the b axis |  |  |
| C14-H14A∙∙∙C9 | 2.8237(8) | 2.8401(33) |
| C14-H14C∙∙∙C6 | 2.7448(8) | 2.7368(32) |
| C10-H10B∙∙∙C6 | 2.8030(9) | 2.8573(28) |
| along the c axis with Cl- anion |  |  |
| N2-H2∙∙∙Cl1 |  | 2.3247(10) |
| N3-H3∙∙∙Cl1 |  | 2.3260(11) |
| C25-H25B∙∙∙Cl1 |  | 2.8952(12) |
| C10-H10A∙∙∙Cl1 |  | 2.7692(12) |
| C22-H22∙∙∙Cl1 |  | 2.7152(12) |
| along the c axis with NO3- anion |  |  |
| N2-H2∙∙∙N5 | 2.5084(5) |  |
| N3-H3∙∙∙O5 | 2.1508(5) |  |
| N2-H2∙∙∙O5 | 2.1830(7) |  |
| N2-H2∙∙∙O6 | 2.1837(6) |  |
| C23-H23B∙∙∙O5 | 2.6410(7) |  |
| C26-H26A∙∙∙O6 | 2.6337(9) |  |
| C25-H25A∙∙∙O7 | 2.4922(7) |  |
| C10-H10A∙∙∙O7 | 2.5018(8) |  |
| C22-H22∙∙∙O7 | 2.4534(7) |  |
| C19-H19∙∙∙O7 | 2.6974(11) |  |
| Plane-plane that anions occupy | 6.372 | 6.008 |

|  |  |
| --- | --- |
|  |  |
| **(a)** | **(b)** |

**Figure S9** Intermolecular interactions related to the anions for (a) **3** and (b) **4** on the same point of view. Detail of the interactions (dotted lines) are presented in Table S3 and Table S4*.* Color code: orange: iron, red: oxygen, dark blue: nitrogen, green: chlorine and grey: carbon. Hydrogen atoms are omitted for clarify

|  |  |
| --- | --- |
|  |  |
| **(a)** | **(b)** |

**Figure S10** (a) the [Fe(3-MeOthsa)2]- anionic molecule of **5** showing all the coordination environment in the octahedral geometry, (b) the [Fe(3-MeOthsa)2]- anionic molecule coordinates to two Cs cations via Cs-O bonds showing high distortion around the Fe(III) metal in **5**

**Table S4** Related Hydrogen bonds in [Fe(3-EtOSalEen)2]NO3 **3** and [Fe(3-EtOSalEen)2]Cl **4** at 100 K

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | H∙∙∙A/Å | X∙∙∙A/Å | ∠ X-H∙∙∙A/° | Note |
| **3** |  |  |  |  |
| C17-H17∙∙∙O1 | 2.6415(9) | 3.5154(12) | 153.147(23) |  |
| C15-H15B∙∙∙C1 | 2.9163(10) | 3.6910(11) | 135.791(31) |  |
| C14-H14A∙∙∙C9 | 2.8237(8) | 3.5556(10) | 132.074(34) |  |
| C14-H14C∙∙∙C6 | 2.7448(8) | 3.4612(9) | 130.383(26) |  |
| C10-H10B∙∙∙C6 | 2.8030(9) | 3.4316(13) | 121.968(19) |  |
| N2-H2∙∙∙N5 | 2.5084(5) | 3.4039(7) | 164.874(23) |  |
| N3-H3∙∙∙O5 | 2.1508(5) | 3.0051(7) | 154.038(30) | Moderate |
| N2-H2∙∙∙O5 | 2.1830(7) | 3.0209(9) | 151.215(22) | Moderate |
| N2-H2∙∙∙O6 | 2.1837(6) | 2.9888(8) | 145.821(26) | Moderate |
| C23-H23B∙∙∙O5 | 2.6410(7) | 3.3875(10) | 132.315(31) |  |
| C26-H26A∙∙∙O6 | 2.6337(9) | 3.4344(11) | 139.039(32) |  |
| C25-H25A∙∙∙O7 | 2.4922(7) | 3.3405(11) | 143.522(39) |  |
| C10-H10A∙∙∙O7 | 2.5018(8) | 3.4456(10) | 159.265(24) |  |
| C22-H22∙∙∙O7 | 2.4534(7) | 3.3541(10) | 158.198(32) |  |
| C19-H19∙∙∙O7 | 2.6974(11) | 3.5283(16) | 146.437(23) |  |
| **4** |  |  |  |  |
| C17-H17∙∙∙O1 | 2.6764(23) | 3.5320(41) | 149.996(220) |  |
| C15-H15B∙∙∙C1 | 2.8379(39) | 3.6515(51) | 112.327(136) |  |
| C14-H14A∙∙∙C9 | 2.8401(33) | 3.6087(56) | 135.878(251) |  |
| C14-H14C∙∙∙C6 | 2.7368(32) | 3.4059(54) | 125.973(246) |  |
| C10-H10B∙∙∙C6 | 2.8573(28) | 3.4790(46) | 121.515(230) |  |
| N2-H2∙∙∙Cl1 | 2.3247(10) | 3.2131(29) | 159.650(164) |  |
| N3-H3∙∙∙Cl1 | 2.3260(11) | 3.2474(33) | 170.595(181) |  |
| C25-H25B∙∙∙Cl1 | 2.8952(12) | 3.6973(35) | 138.692(188) |  |
| C10-H10A∙∙∙Cl1 | 2.7692(12) | 3.7459(40) | 169.261(208) |  |
| C22-H22∙∙∙Cl1 | 2.7152(12) | 3.5677(34) | 149.744(180) |  |

Most of the interactions are weak hydrogen bonds.

**Table S5** Comparison of the P4AE interactions in **3** and **4** with the related [Fe(3-OMe-SalEen)2] cations and their SCO features

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| P4AE | **3** | **4** | [Fe(3-OMe-SalEen)2][Ni(dmit)2][2] | [Fe(3-OMe-SalEen)2]ClO4[3] | [Fe(3-OMe-SalEen)2]PF6[4] |
| π-π | 3.258 | 3.245 | 180 K = 3.290, 290 K = 3.357 | 90 K = 3.286, 298 K = 3.338 | 120 K = 3.299,  200 K = 3.352,  300 K = 3.405 |
| C18-H18∙∙∙π | 2.766 | 2.752 | 180 K = 3.064, 290 K = 3.066 | 90 K = 2.816, 298 K = 2.929 | 120 K = 2.807,  200 K = 3.003,  300 K = 3.039 |
| SCO | 50% | Incomplete | 1st cycle onlyT ↑ = 345  T↓ = 275 | 196 | T↓ = 162.5 K, T ↑ = 165.5 K |
|  | Abrupt | Gradual | Gradual | Abrupt SCO | Abrupt SCO |

Note there are no examples of[Fe(3-EtO-SalEen)2] cations published previously. Comparison are made to the closestrelated system which is [Fe(3-OMe-SalEen)2]+

**Table S6** Cs-O bond lengths in **5** and **6**

|  |  |  |  |
| --- | --- | --- | --- |
|  | |  | |
| Compound **5** | | Compound **6** | |
| Cs1—O1/Å | 3.1052 (16) | Cs1—O5/Å | 3.178 (6) |
| Cs1—O2/Å | 3.1249 (18) | Cs1—O9/Å | 3.071 (7) |
| Cs1—O3/Å | 2.972 (5) | Cs1—O1/Å | 3.111(6) |
|  |  | Cs2—O3/Å | 3.309 (9) |
|  | | Cs2—O7/Å | 3.31 (2) |
|  | | Cs2—O8/Å | 2.792 (4) |

Covalent Radii/Å; O = 0.660 Å, Cs = 2.650 Å

**Table S7** Intermolecular interactions in CsH2O[Fe(3-MeOthsa)2] **5** at 123 K

|  |  |
| --- | --- |
| Connect a polymeric chain in ac plane | Å |
| N3-H3B∙∙∙π | 3.093 |
| N3-H3B∙∙∙S1 | 2.7800(7) |
| N3∙∙∙S1 | 3.4492(22) |
| ∠ N3-H3B∙∙∙/S1° | 133.901(138) |

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**Figure S11** N-H∙∙∙π and N-H∙∙∙S interactions connecting a 1D polymer chain of **5** in a pseudo-3D structure

|  |  |
| --- | --- |
|  |  |
| **(a)** | **(b)** |
|  |  |

**Figure S12** (a) Representation of a Cs1∙∙∙Cs1 polymeric chain viewed along the c axis, and (b) the [Fe(5-NO2thsa)2]+ bridging between Cs1 and Cs2 moieties.

## **References**

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