The handle [http://hdl.handle.net/1887/26519](http://hdl.handle.net/1887/26519) holds various files of this Leiden University dissertation.

**Author:** Zheng, Sipeng  
**Title:** Mononuclear spin-transition materials based on the bapbpy scaffold  
**Issue Date:** 2014-06-25
Increasing the transition temperature of bapbpy-based mononuclear spin-crossover compounds: interplay between molecular and crystal engineering

Abstract

In this chapter, it is shown that different isomers of the same mononuclear iron(II) complex give materials with different spin crossover properties, and that minor modifications of the bapbpy ligand allows for obtaining spin crossover (SCO) near room temperature. A qualitative model is provided to understand the link between the structure of bapbpy-based ligands and the SCO properties of their iron(II) compounds. Thus, seven new trans-[Fe(R₂bapbpy)(NCS)₂] compounds are reported, where the R₂bapbpy ligand bears picoline (9-12), quin-2-oline (13), isoquin-3-oline (14) or isoquin-1-oline (15) substituents. From this series, three compounds (12, 14 and 15) have SCO properties; for 15 the SCO occurs at 288 K. The crystal structures of compounds 11, 12 and 15 show similar intermolecular interactions to those found in the parent compound [Fe(bapbpy)(NCS)₂] (1), in which each iron complex interacts with its neighbours via N–H···S hydrogen bonding and π–π stacking. For compounds 12 and 15 hindering groups located near the N–H bridges weaken the N···S intermolecular interactions, resulting in non-cooperative SCO. For compound 14, the substitution is further away from the N–H bridges and the SCO remains cooperative as in 1 with a hysteresis cycle. Optical microscopy pictures show the strikingly different spatio-temporal evolution of the phase transition in the non-cooperative SCO compound 12, compared to that found in 1. Heat capacity measurements were made for compounds 1, 12,
and 15 and fitted to the Sorai domain model. The number \( n \) of like-spin SCO centres per interacting domain, which is related to the cooperativity of the spin transition, was found to be high for compounds 1 and 14 and low for compounds 12 and 15. Finally, it is found that although the compounds 11-12 and 14-15 are pairs of isomers their SCO properties are surprisingly different.

### 2.1. Introduction

Iron-based spin crossover (hereafter, SCO) compounds are recognized as highly promising switchable molecular materials,\(^1\)-\(^4\) with potential applications in information storage,\(^5\), \(^6\) image display,\(^7\) gas\(^8\), \(^9\) or temperature sensors.\(^10\) The structure-function relationship for iron(II)-based SCO compounds has been under discussion for several decades, as it would be remarkable to design \textit{de novo} an SCO material with pre-defined magnetic properties. In particular, many applications would ideally require materials for which SCO transitions occur near room temperature.\(^11\) The occurrence of cooperative SCO with hysteresis loops is also thought to be critical for information storage applications, as it allows both low spin and high spin (hereafter, LS and HS) states to be populated at one defined temperature.\(^12\), \(^13\) The occurrence of the spin transition is an inherent property of the ligand field strength created by the ligand set around the metal centre;\(^14\) thus, transition temperatures should ideally be tunable by molecular-engineering approaches. Cooperativity is the result of a combination of short- and long-range interactions between individual molecules in the solid state. There are several quantitative models for cooperativity based on the mean-field approach,\(^15\) elastic\(^16\)-\(^19\) or electrostatic\(^20\) interactions. However, such models only allow for rationalization of the magnetic behaviour of SCO compounds after the compounds have been synthesized and their properties measured.\(^12\) Thus, a qualitative approach based on molecular engineering is still required in the search of new SCO materials.

The mononuclear SCO compound [Fe(bapbpy)(NCS)\(_2\)] (compound 1; bapbpy = \(N,N'\)-di(pyrid-2-yl)-2,2'-bipyridine-6,6'-diamine, see Scheme 2.1)\(^21\) was shown to be highly cooperative. Its two-step spin crossover features a rather unusual ordered intermediate [HS-LS-LS] phase that is stable over a surprisingly large temperature range.\(^12\), \(^22\), \(^23\) Unfortunately, both transition temperatures for this material are too low for any practical applications. Thus, we considered modifying the bapbpy ligand to increase the stability of the LS phase. Seven new trans-[Fe(R2-bapbpy)(NCS)\(_2\)] complexes were then synthesized (Table 2.1), and their SCO properties investigated.
2.2. Results

The ε,ε’ (2), δ,δ’ (3), γ,γ’ (4), and β,β’ (5) isomers of 6,6’-bis[N-(methyl-2-pyridyl)amino]-2,2’-bipyridine (Me₂bapbpy) were synthesized by a palladium-catalyzed Buchwald-Hartwig coupling reaction that involves the corresponding methyl-substituted α-aminopyridine and 2,2’-dibromo-6,6’-bipyridine, using KO⁻Bu as a base (Scheme 2.2). Under the same reaction conditions, the use of quinolin-2-amine, isoquinolin-3-amine and isoquinolin-1-amine led to ligands 6, 7 and 8, respectively.

Scheme 2.1. Representations of the ligand bapbpy and its disubstituted derivatives 2-8.

Scheme 2.2. Synthesis route for bapbpy derivatives 2 to 8. 2 mol% Pd(dba)₂ and 4 mol% (S)-BINAP was used.
Coordination of ligands 2-8 to iron(II) thiocyanate was achieved in methanol at room temperature overnight, which leads to compounds 9 to 15, respectively (see formulae in Table 2.1). As neither the free ligands nor their iron complexes are soluble in methanol, Fe(NCS)₂ was introduced in excess amount, and the complexes were filtered and washed with methanol after the reaction to remove the excess amount of metal precursor. The materials were analyzed by IR spectroscopy, magnetic susceptibility measurements, mass spectrometry, ¹H NMR in DMSO-d⁶, and for some of them (10, 11, 12, and 15) by X-ray crystallography and elemental analysis. The IR spectra of the seven solids show the characteristic stretching vibrations of the coordinated thiocyanate ligands (see Table 2.1). By electron-spray mass spectrometry, all compounds showed the molecular peak that corresponds to the monocation [Fe(R₂bapbpy)(NCS)]⁺ (calculated at m/z = 482.08 for 9-12, and 554.09 for 13-15, see Experimental Part).

Table 2.1. Formulae and infrared thiocyanate stretching vibrations for compounds 9-15.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>NCS⁻ vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>trans-[Fe(2)(NCS)₂]</td>
<td>2056</td>
</tr>
<tr>
<td>10</td>
<td>trans-[Fe(3)(NCS)₂]</td>
<td>2061 (s), 2093 (m)</td>
</tr>
<tr>
<td>11</td>
<td>trans-[Fe(4)(NCS)₂]</td>
<td>2075</td>
</tr>
<tr>
<td>12</td>
<td>trans-[Fe(5)(NCS)₂]</td>
<td>2063</td>
</tr>
<tr>
<td>13</td>
<td>trans-[Fe(6)(NCS)₂]</td>
<td>2036</td>
</tr>
<tr>
<td>14</td>
<td>trans-[Fe(7)(NCS)₂]</td>
<td>2062</td>
</tr>
<tr>
<td>15</td>
<td>trans-[Fe(8)(NCS)₂]</td>
<td>2071 (s), 2110 (m)</td>
</tr>
</tbody>
</table>

The temperature dependence of the χₘT product, in which χₘ stands for the molar magnetic susceptibility and T the temperature, was measured for compounds 9-15 in the range 5-300 K, both in the cooling and in the heating modes. The magnetic measurements show that complexes 9, 10, 11 and 13 are in the high-spin (HS) state throughout the whole temperature range, with room-temperature χₘT values that range from 2.7 to 3.4 cm³ K mol⁻¹, and a decrease of χₘT below 50 K is a typical feature of a zero-field splitting. The data for compound 11 are shown in Figure 2.1 as an example. Unlike for compounds 9-11 and 13, the crude powder of compound 12 shows a reversible colour change, that is, a rusty colour near room temperature but a dark red
colour at liquid nitrogen temperature, which suggests a reversible spin crossover. As shown in Figure 2.1, the room-temperature $\chi_M T$ value of about 3.5 cm$^3$ K mol$^{-1}$ remains relatively constant in the temperature range of 275-300 K and indicates an HS Fe(II) species in an octahedral coordination environment.\textsuperscript{25} In the range 125-275 K the $\chi_M T$ value diminishes gradually to reach 0.05 cm$^3$ K mol$^{-1}$; it remains close to zero in the range 5-125 K. The transition temperature for compound 12, determined as the maximum of $d(\chi_M T)/dT$, was found to be 170(2) K.

For isoquinolin-3-amino compound 14, a similar colour change between room-temperature and liquid-nitrogen temperature is observed, however, the evolution of $\chi_M T$ as a function of $T$ shows different features (Figure 2.1). From 3.51 cm$^3$ K mol$^{-1}$ at 300 K the value of $\chi_M T$ remains roughly constant until 135 K, at which point it quickly drops to 0.85 cm$^3$ K mol$^{-1}$ at 75 K. The transition temperature $T_{1/2\downarrow} = 113(2)$ K was derived at the maximum of $d(\chi_M T)/dT$ vs. $T$ in the cooling mode. The residual HS fraction remains roughly constant between 75 and 5 K, at which point the value of $\chi_M T$ is 0.63 cm$^3$ K mol$^{-1}$. In the heating mode the transition temperature $T_{1/2\uparrow}$ is higher than $T_{1/2\downarrow}$ [$T_{1/2\uparrow} = 125(2)$ K], that is, the SCO behaviour of compound 14 is cooperative and shows a hysteresis loop characterized by a $\Delta T_{hyst}$ of approximately 11(3) K.

For isoquinolin-1-amino compound 15, the colour of the crude powder near room temperature is significantly darker than that of compound 11, 12 or 14, but heating the powder under argon allowed for reversibly obtaining the lighter orange colour typical for HS iron(II) compounds based on the bapbpy manifold. Magnetic susceptibility measurements above room temperature confirmed the spin crossover of compound 15, as the value of $\chi_M T$ gradually decreased from 3.34 cm$^3$ K mol$^{-1}$ at 396 K (the upper limit of our SQUID magnetometer) down to 0.29 cm$^3$ K mol$^{-1}$ at 80 K. The spin crossover was found to occur over a large $T$ range of more than 150 K without any hysteresis loop, which suggests non-cooperative behaviour. The transition temperature for the spin transition, defined as the maximum of $d(\chi_M T)/dT$ vs. $T$, was estimated to be 288(5) K, which is the highest reported transition temperature for all of the bapbpy-based iron compounds synthesized so far, and very close to room temperature.
Figure 2.1. Plot of $\chi_M T$ vs. $T$ for compounds 11, 12, 14 and 15. There is no apparent hysteresis loop in the spin crossover for compounds 12 and 15. The dashed line represents magnetic data for powder samples of compound 1.\textsuperscript{22}

Single crystals suitable for X-ray structure determination were obtained for complexes 10, 11, 12 and 15 by liquid-liquid diffusion method: for compounds 11, 12 and 15, methanol was diffused into a solution of the complex in DMF, whereas for compound 10 the ligand 3 was first dissolved in DMF, followed by layering of 1.1 eq of Fe(NCS)\textsubscript{2} and methanol. In all cases, single crystals appeared after three days. The structures of compounds 10 and 11 (HS only) was determined at 110 K. The structures of the SCO compounds 12 and 15 were determined both at 110 (LS) and near 295 K (HS for 12, HS+LS for 15) since no significant loss of crystallinity occurred when the crystals underwent the spin transition. The crystal lattice does not contain any solvent molecules in each structure, and the crystal structures are shown in Figure 2.2. A selected set of geometrical parameters is provided in Table 2.2. In all cases, the substituted ligands R\textsubscript{2}bapbp coordinate iron(II) in the basal plane of the coordination
Figure 2.2. Displacement ellipsoid plots (50% probability level) at 110(2) K for compounds 10 and 11 in the HS state, and for compounds 12 and 15 in the LS state. Selected labelling is only shown for crystallographically independent atoms. Hydrogen atoms were omitted for clarity.

sphere, thus leaving the two thiocyanate anions in *trans* positions.

Compound 10 crystallizes in the triclinic space group *P*-1. The average Fe–N bond length is found at 2.16 Å, which is typical of an HS Fe(II) complex in an FeN₆ octahedral environment. The basal coordination angles vary from 77.05(6)° to 115.78(6)° (Table 2.2), and the torsion angles of [N1–N3–N4–N6 = 23.66(7)°] and [C1–N1–N6–C22 = 48.27(1)°], indicating a strong distortion of the octahedral geometry. The compounds 11, 12 and 15 crystallize in the centrosymmetric *C*₂/c space group, and the iron centres are found at twofold rotation axes running through Fe1 and the middle of the central C–C bond of the ligand. As a result, only one half of the molecule is crystallographically independent (*i.e.*, *Z’* = 0.5). Like in complex 1 the octahedrons are significantly distorted so that the two facing hydrogen atoms located in an *ɛ* position on each substituted pyridine ring cannot be in contact. For complexes 12
Table 2.2. Selected bond distances (Å) and angles (°) for the HS phase of 10, 11 and for the two phases of 12 and 15.

<table>
<thead>
<tr>
<th>Compound</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>110(2)</td>
<td>110(2)</td>
<td>295(2)</td>
<td>110(2)</td>
</tr>
<tr>
<td>Phase</td>
<td>HS</td>
<td>HS</td>
<td>HS</td>
<td>LS</td>
</tr>
<tr>
<td>Fe1−N1</td>
<td>2.155(1)</td>
<td>Fe1−N1</td>
<td>2.1436(15)</td>
<td>2.1490(14)</td>
</tr>
<tr>
<td>Fe1−N3</td>
<td>2.161(1)</td>
<td>Fe1−N3</td>
<td>2.1540(16)</td>
<td>2.1273(13)</td>
</tr>
<tr>
<td>Fe1−N4</td>
<td>2.156(1)</td>
<td>Fe1−N4</td>
<td>2.1724(16)</td>
<td>2.1542(16)</td>
</tr>
<tr>
<td>Fe1−N6</td>
<td>2.170(1)</td>
<td>N1−Fe1−N1</td>
<td>113.75(8)</td>
<td>110.90(8)</td>
</tr>
<tr>
<td>Fe1−N7</td>
<td>2.144(2)</td>
<td>N1−Fe1−N4</td>
<td>86.21(6)</td>
<td>86.98(6)</td>
</tr>
<tr>
<td>Fe1−N8</td>
<td>2.176(2)</td>
<td>N3−Fe1−N1</td>
<td>85.83(6)</td>
<td>86.28(5)</td>
</tr>
<tr>
<td>N1−Fe−N6</td>
<td>115.78(6)</td>
<td>N3−Fe1−N3</td>
<td>76.96(9)</td>
<td>78.40(7)</td>
</tr>
<tr>
<td>N3−Fe1−N1</td>
<td>85.24(6)</td>
<td>N3−Fe1−N4</td>
<td>87.72(6)</td>
<td>83.19(6)</td>
</tr>
<tr>
<td>N4−Fe1−N3</td>
<td>77.05(6)</td>
<td>N4−Fe1−N4</td>
<td>162.48(9)</td>
<td>179.25(9)</td>
</tr>
<tr>
<td>N6−Fe1−N4</td>
<td>85.23(6)</td>
<td>Cg2⋯Cg1’</td>
<td>3.934(9)</td>
<td>3.802(9)</td>
</tr>
<tr>
<td>N7−Fe1−N8</td>
<td>166.17(6)</td>
<td>Cg5⋯Cg1’</td>
<td>n. a.</td>
<td>n. a.</td>
</tr>
<tr>
<td>N1−N3−N4−N6</td>
<td>23.66(7)</td>
<td>N2⋯S1</td>
<td>3.4592(17)</td>
<td>4.1605(16)</td>
</tr>
<tr>
<td>N2⋯S2’</td>
<td>3.410(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N5’⋯S2’</td>
<td>3.403(2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cg3⋯Cg4’</td>
<td>3.921(10)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

n. a. = not applicable. Symmetry operator * = -x, -y, -z

and 15 the average Fe−N bond distance at 110 K is around 1.97-1.98 Å, which is characteristic of an LS Fe(II) complex in an FeN₆ octahedral environment. For compound 11 at 110 K and for compound 12 at 295 K, the average Fe−N bond distance is approximately 2.14-2.16 Å, whereas it is shorter (~2.07 Å) for complex 15 at 300 K. The latter value is intermediate between those expected for a pure HS and a pure LS Fe(II) centres. This observation is in good agreement with the magnetic susceptibility measurements, which indicate that the SCO is only half-way done at 295 K. Finally, the X-ray diffraction measurements confirm the spin crossovers for compounds 12 and 15. A bond-length analysis for the HS state shows that the Fe1−N3 and Fe1−N4 bond lengths [2.1350(15) and 2.1481(18) Å, respectively], which involve the bipyridine
chelate and the thiocyanate ions, respectively, are generally longer for compound 11 than for compound 12 (see Table 2.2) or 1. In the LS state, longer Fe–N bonds would account for a weaker ligand field splitting; however in the HS state such conclusion cannot be drawn, because two electrons are located in antibonding orbitals. The absence of spin crossover for compound 11 remains intriguing (see Discussion).

The crystal packing of compounds 10, 11, 12 and 15, like for 1, are characterized by two sets of ‘‘supramolecular’’ interactions found along one-dimensional crystallographic direction (that is, the c axis). The first set includes N–H···S hydrogen bonds. For compounds 11, 12 and 15, the N–H bridges of each tetrapyridyl ligand are donors to the thiocyanate ions of two neighbouring complexes (see Figure 2.3). The N···S intermolecular distances are shorter for compound 11 [3.459(2) Å], and are comparable to those found in the HS phase of compound 1 [3.424(2) Å]. By contrast, these distances are significantly longer for the near-room temperature structures of compound 12 [4.160(2) Å] and 15 [3.932(4) Å], indicating weaker N–H···S intermolecular interactions. Remarkably, compound 10 shows a different N−H···S network, where the S atom (Figure 2.3) on one thiocyanate ligand is accepting two N−H···S hydrogen bonds of the NH bridges from two neighbouring molecules. The corresponding N···S intermolecular distances are the shortest within this family of compounds [3.403(2) Å and 3.410(2) Å at 110 K].

The second set of intermolecular interactions includes π−π stacking between the terminal pyridine rings of two adjacent molecules, as shown in Figure 2.3. The centroid-centroid distances are 3.921(10), 3.934(9) and 3.8018(9) Å for compounds 10, 11 and 12 respectively. Such distances are similar to that found in compound 1 [3.881(1) Å]. For compound 15, each ring of the bipyridine fragment is involved in π−π stacking with the two fused aromatic rings of the isoquinoline groups of the neighbouring molecule, with centroid-centroid distances of 3.798(6) and 3.867(13) Å. Overall, π−π stacking interactions are similar within this family of compounds (that is, 1, 10, 11, 12 and 15). There seems to be no obvious correlation between the cooperativity of the SCO and the π−π stacking interactions in the solid state.
Figure 2.3. Crystal packing along the crystallographic $c$ axis for compounds 10, 11, 12 and 15. Distances are given for the HS (10, 11 and 12) and LS + HS (15) phases.

In addition, two sets of data aimed at investigating the temperature dependence of the unit cell dimensions for 12 were collected between 150 and 250 K at ± 5 K intervals.
for both cooling and heating regimes (data not shown), and from 290 to 110 K at −10 K intervals (see Figure 2.4). The first set shows no sign of hysteresis loop in the cell parameters between the cooling and heating regimes. The second set (see Figure 2.4) shows a continuous decrease of $V/Z$ (that is, volume per formula unit) over a large temperature range as $T$ decreases. The drop in $V/Z$ is more pronounced between 140 and 240 K. Overall, temperature dependence of the unit cell dimensions for 12 is consistent with the results of the magnetic susceptibility measurements.

Figure 2.4. Plot of the volume per formula unit $V/Z$ ($\text{Å}^3$) versus $T$ (K) for compound 12. Values of $V/Z$ are measured for the cooling transition HS $\rightarrow$ LS at −10 K intervals.

The SCO transition of Fe(II) compounds in the solid state usually leaves clear signatures in calorimetric measurements, especially in the case of abrupt or cooperative SCO, for which sharp heat capacity peaks are detected. Molar heat capacities were determined at constant pressure, $C_p$, of compounds 12, 14 and 15 from differential scanning calorimetry (DSC) experiments. For comparison molar heat capacity for a powder sample of compound 1 is also given, for which DSC traces and excess enthalpy and entropy due to the SCO ($\Delta_{SCO}H$ and $\Delta_{SCO}S$) were previously reported.\textsuperscript{21, 22} The results are given in Figure 2.5. The excess heat capacity, $\Delta C_p$, due to the spin-crossover phenomenon in these compounds (shown in Figure 2.6) is obtained by estimating normal heat capacity curves with the high and low temperature data, which are
represented as dashed lines in Figure 2.5, and subtracting it from the total heat capacity. In this estimation no heat capacity step at the transition temperature was considered. The deduced calorimetric values associated with the SCO $\Delta_{SCO}H$ (integration of $\Delta C_p$ over $T$) and $\Delta_{SCO}S$ (integration of $\Delta C_p$ over $\ln T$) are gathered in Table 2.3.

Figure 2.5. Molar heat capacities of compounds 1, 12, 14 and 15 upon warming. Dashed lines are estimated normal heat capacities used for $\Delta C_p$ determination. Data for 1 is taken from reference 21.

Figure 2.6. Excess heat capacity associated to the SCO transitions for compounds 1, 12, 14 and 15 upon warming. The full lines are the best fit to the domain model of Sorai, as described in the text.
Table 2.3. Excess enthalpy and entropy due to the SCO, and parameters describing the SCO \( T_{1/2} \) and its cooperativity \( (n) \) in compounds 1, 12, 14 and 15 as derived from the domain model (see text).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta_{SCO}H ) (kJ mol(^{-1}))</th>
<th>( n )</th>
<th>( T_{1/2} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.85 / 8.65</td>
<td>11.6 / 22.5</td>
<td>192 / 221</td>
</tr>
<tr>
<td>12</td>
<td>6.01</td>
<td>2.8</td>
<td>185</td>
</tr>
<tr>
<td>14</td>
<td>2.73</td>
<td>16.8</td>
<td>125</td>
</tr>
<tr>
<td>15</td>
<td>8.91</td>
<td>5.3</td>
<td>287</td>
</tr>
</tbody>
</table>

\( a \) In the case of compound 1, the two numbers given refer to the two steps observed in the SCO, while the enthalpies and entropies are given per mole of transiting Fe(II) centre for better comparison with single-step SCO compounds.

Compounds 12 and 15 present very broad heat capacity anomalies at temperatures comparable to the transition temperatures determined by the magnetic susceptibility measurements, that is, centred on 185 and 287 K, respectively. For both compounds no significant difference is found in molar heat capacities when the samples are either warmed or cooled. On the other hand, compound 14 exhibits one sharp heat capacity peak centred on 125 K, in excellent agreement with the magnetic measurements. Although large values of \( \Delta_{SCO}H \) and especially \( \Delta_{SCO}S \) (typically when largely surpassing the purely electronic entropy change \( \Delta S = R \ln[(2S_{HS} + 1)/(2S_{LS} + 1)] = 13.45 \text{ J mol}^{-1} \text{ K}^{-1} \)) are often taken as an indication of cooperativity, these values depend on the actual temperature at which the SCO takes place. It is thus rather difficult to make comparisons between compounds for which SCO transitions occur over different temperature ranges. To quantify and to compare the cooperative character of the SCO compounds presented in this work, we considered the phenomenological domain model proposed by Sorai, which has been widely used when accurate calorimetric data are available.\(^{26}\) This model is based on heterophase fluctuations and gives a measure of cooperativity through the number \( n \) of like-spin SCO centres per interacting domain. The larger the domains are, the more cooperative the transition is. Compounds that show a gradual SCO usually give \( n \) values close to 1,\(^{27,28}\) whereas values as large as 95 have been derived for the prototype cooperative SCO complex [Fe(phen)\(_2\)(NCS)\(_2\)] (phen = 1,10-phenanthroline).\(^{29}\) According to this model, the excess heat capacity \( \Delta C_P \) can be written as in Equation 2.1.
\[
\Delta C_p = \frac{n(\Delta_{SCO}H)^2}{RT^2} \exp \left\{ \frac{n\Delta_{SCO}H}{R} \left( \frac{1}{T} - \frac{1}{T_{1/2}} \right) \right\} \left\{ 1 + \exp \left[ \frac{n\Delta_{SCO}H}{R} \left( \frac{1}{T} - \frac{1}{T_{1/2}} \right) \right] \right\}^2
\]

Eq 2.1

The experimental \( \Delta C_p \) data (see Figure 2.6) were very satisfactorily fit to Equation 2.1 using \( \Delta_{SCO}H \) as derived from DSC experiments but leaving \( T_{v2} \) free. In the case of compound 1, two separate values of \( n \) and \( \Delta_{SCO}H \) were used for each step. The resulting values for \( n \) are given in Table 2.3, and clearly correlate with the differences in abruptness of the SCO curves in magnetic susceptibility measurements or sharpness of heat capacity peaks in DSC. Both compounds 1 (especially the high temperature step) and 14 can be considered as cooperative SCO compounds with values of \( n \) of 22.5 and 16.8, respectively, whereas compounds 12 and 15 have low \( n \) values (2.8 and 5.3, respectively) and can be considered as poorly cooperative.

In line with this domain model, it is interesting to note that the colour changes occur in a very different manner for compounds 1 or 12, correlating with the cooperativity of the spin-crossover process. Figure 2.7a displays bright-field images at five different temperatures in the cooling mode of a single crystal of compound 1. At 233 K the crystal is totally in the HS state (red) and at 228 K it is totally in the intermediate phase (hereafter, IP, dark red). At 231 K one can clearly observe the epitaxic relation between the mother (HS) and daughter (IP) phases characterized by an obvious front, which indicates the first-order character of this transition. By decreasing the temperature to 229 K this new phase propagates along the \( c \) axis of the crystal – similar to what was reported by Bedoui et al.23 Figure 2.7b presents bright field images of a single crystal of 12 in the cooling mode. At 293 K the crystal is totally in the HS state, and at 120 K it is totally in the LS state. By lowering the temperature from 293 K to 120 K the crystal colour changes slowly from red to dark red, but here in a continuous and homogenous manner without any observable epitaxic relation between the mother and daughter phases. In line with the very continuous evolution of \( V/Z \) and \( \chi_M T \) as a function of \( T \), the spatiotemporal evolution of the SCO does not involve any observable phase separation and – within the limits of the experimental resolution – the sample seems to behave as a homogenous mixture of the HS and LS phases at intermediate
temperatures. The reproducibility of the observed phenomena has been confirmed using several other crystals.

Figure 2.7. Bright-field optical microscopy images of single crystals of (a) 1 and (b) 12 recorded upon cooling in transmission mode.

2.3. Discussion

Ideally, the transition temperature of a spin-crossover material depends mostly on the ligand field created around iron(II) by the ligand set, whereas the cooperativity of the spin crossover depends on how molecules interact with each other in the solid state. To a certain extent, the new materials described in this study help to provide a qualitative model for the structure-property relationship of bapbpy-based SCO materials. The absence of uncoordinated counter anions and uncoordinated solvent molecules in the crystal lattice is beneficial in that respect.

Intermolecular N–H···S hydrogen bonds seem to be critical for the cooperativity of iron(II)-based bapbpy derivatives. In a previous study, we have shown that the solvated compound [Fe(bapbpy)(NCS)$_2$]:2DMF is a non-cooperative SCO system, and that the uncoordinated DMF molecules are hydrogen-bonded to the N–H bridges of the ligand. In this work, the crystal structures of compounds 12 and 15 clearly show that the existence of hindering groups in the β positions results in longer N···S distances. This structural feature is associated with a low cooperativity of the spin crossover in both cases, as shown by magnetic, thermal, single crystal X-ray diffraction and optical microscopy data. As the β substituents point in the same direction as that of the N–H bonds, they seem to contribute to weakening of the intermolecular N–H···S interactions between two adjacent molecules (see Scheme 2.3a), which may explain the lower cooperativity of these two materials. In contrast, the SCO behaviour of compound 14 is
found to be cooperative as has been observed for compound 1, with discontinuous spin transitions associated with hysteresis cycles. We associate such cooperativity to the absence of any substituent in the β position. Although the solubility of compound 14 in DMF was too low to grow single crystals, one may predict short N⋯S intermolecular distances (that is, < 3.6 Å).

Scheme 2.3. Intermolecular vs. intramolecular steric hindrance for substituted bapbpy iron(II) SCO compounds. a) with substituents in β positions, steric bulk results in long N−H⋯S hydrogen bonds, and thus low cooperativity for the SCO; b) with substituents in ε positions, intramolecular steric hindrance results in larger distortions in the equatorial plane, lowering splitting of the ligand field, thus stabilizing the HS state.

The transition temperatures ($T_{1/2}$) of an SCO compound may be tuned by changing the electronic and steric properties of the ligand. In the case where the transition temperature is too low or the compound is always HS, one possibility would be to increase the ligand field strength. In contrast, when the ligand field strength is lowered, an HS state will be favoured. For compounds 9, 10 and 13, each terminal pyridyl group bears a hindering substituent in the ε and/or δ position. Due to the embracing nature of this family of ligands, one might expect that intramolecular steric hindrance between these two facing substituents would lower the ligand field splitting of the complex by increasing the distortions of the organic backbone (see Scheme 2.3b). Thus, iron bis(thiocyanate) compounds based on ligands 2, 3 and 6 are expected to remain in the HS state, which is indeed observed experimentally.

Consistently, we might expect compounds 11, 12, 14 and 15 to have SCO properties because they do not have substituents in the ε or δ position. The fact that compound 12 shows SCO properties whereas compound 11 does not, is hence a surprise. Based on the Hammett constants a methyl substituent is considered to be slightly more
electron-donating in the para position ($\sigma_p = -0.17$) than in the meta position ($\sigma_m = -0.07$), which, from a molecular engineering point of view, should favour an LS state for 11. There must hence be subtle crystal packing effects that counter-balance this trend and lower the crystal field parameter of the molecule once packed in the crystal lattice. Similar exceptions have been described in the literature, for example by Gómez-García et al., who explained the absence of SCO for $[\text{Fe(abpt)}_2(\text{tcnome})_2]$ (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole; tcnome$^- = 1,1,3,3$-tetracyano-2-methoxypropenide anion) by a change in the $\pi-\pi$ stacking mode compared to similar $[\text{Fe(abpt)}_2(X)_2]$ compounds with different apical X anions. Analysis of the crystal structures of the HS phases of 11 and 12 shows that the $\pi-\pi$ stacking modes are similar in compounds 11, 12, and 15, but that there are noticeable differences in the orientations of the two NCS$^-$ anions for both compounds (see Figure 2.8a), which might play a role in terms of the crystal field strength of both compounds and hence their ability to undergo SCO. The angles between the mean molecular plane of N3−N1−N1−N3 and the thiocyanate ligand N4−C11−S1 are 66.6 and 77.4°, respectively, for the HS phases of compounds 11 and 12. The deviation from perpendicularity between the NCS$^-$ anions and the mean molecular plane formed by the four basal N atoms is more pronounced for compound 11 due to short contacts between the NCS$^-$ ions and the methyl groups in the $\gamma, \gamma'$ positions of adjacent molecules (see Figure 2.8b, the intermolecular distance C11⋯C12 is 3.29 Å). The bulkiness of these methyl groups promotes a more oblique orientation of the NCS$^-$ anions. By contrast, the crystal packing of 12 shows no such contacts (Figure 2.8b, the intermolecular distances C11⋯C12 and C3⋯C11 are 3.65 and 3.98 Å, respectively). Our current hypothesis is that such intermolecular steric effects may lower the ligand field splitting, and thus the HS state is favoured for compound 11. However, more theoretical insights into the influence of thiocyanate coordination on the crystal field parameter would be required to draw any final conclusions.

As already discussed for compound 1, the presence of a hysteresis cycle in the magnetic susceptibility curve (Figure 2.1) and the intense and sharp peaks observed in DSC (Figure 2.5) indicative of a first-order character for the transition of compound 14. For first-order transitions, the first derivative of the Gibbs free energy is discontinuous, which implies that the enthalpy, the entropy and the volume must be discontinuous at the transition point. Meanwhile, the large values of $n$ derived for these compounds when modelling excess heat capacity data with Sorai’s domain model clearly indicate a
cooperative abrupt SCO. For compounds 12 and 15, the continuous evolution of $V/Z$ and $\chi_M T$ with temperature agree well with the broad humps in $C_p$ vs. $T$ data and the derived low values of $n$, all of which point to gradual continuous SCO. The absence of discontinuity in $V/Z$ at the transition for compound 12 and of hysteresis for both compounds 12 and 15 are clearly contradictory with a first-order transition. For purely second-order transitions however, the first derivative of the Gibbs free energy is continuous, which implies that the enthalpy, entropy and volume are continuous at the transition point, but their second derivative is discontinuous, and hence $\Delta C_p$ is non-zero. The large overall $\Delta_{SCO} H$ and $\Delta_{SCO} S$ that are still derived experimentally for these less-cooperative compounds (see Table 2.3), leaving us with the conclusion that the order for such transitions is neither purely first nor purely second-order.

**Figure 2.8.** a) The different orientation of the thiocyanate ligands relative to the FeN$_4$ coordination plane, shown with a MOLDEN-generated superposition of the geometries of compounds 11 (blue) and 12 (red) in the HS state (according to crystal structures). b) CPK view of two adjacent molecules of 11 (top) and 12 (bottom) in the crystal structure, viewed perpendicularly to the average plane N1–C1–C2–C3–C4–C5.
2.4. Conclusion

A striking feature of the data presented herein is that different isomers of the same mononuclear iron(II) complex give materials with very different SCO properties. Studying these different materials provides valuable insights into the structure-function relationship for bapbpy-based spin crossover iron(II) compounds. First, all bapbpy-based compounds studied in this work are robust materials, for which crystals withstand cooling and heating cycles without substantial modification of their crystallinity or magnetic properties. All crystal lattices are solvent free provided that they are crystallized from DMF/MeOH mixtures. In addition, X-ray crystallography shows that they are all mononuclear with similar crystal packing, which features hydrogen-bond networks through intermolecular N–H⋯S interactions. For SCO compounds the strength of these N–H⋯S hydrogen bonds correlates well with the cooperativity of the spin transition. Compound 11 however represents a counter-example, as its crystal structure exhibit strong N–H⋯S networks but the compound shows no SCO transition.

The information gathered in this work is highly valuable for material design. However, the mere occurrence of SCO, as well as the transition temperatures, are more erratic and therefore difficult to control. For example the difference in transition temperatures between compounds 14 and 15 is very large (ΔT_{1/2} ≈ 169 K), which is surprising considering that they are built from two isomers of the same molecule. Compounds 11 and 12 provide other examples for which there is a significant influence of packing effects on the molecular crystal field strength and on the ability of an apparently suitable ligand to generate spin-crossover Fe(II) compounds. Last but not least, the near room-temperature transition found for compound 15 is promising, provided it can be combined with a higher cooperativity.

2.5. Experimental

2.5.1. General information

All reactions were performed under argon atmosphere using standard schlenk flask and vacuum line techniques. Toluene was dried over sodium and degassed, diethylether was dried over sodium and benzophenone, DMF was dried over CaH₂. 6,6’-dibromo-2,2’-bipyridine was synthesized in two steps according to the literature. All others reagents from commercial sources were used without further purification. 0.1 M methanolic solution
of [Fe(NCS)_2] used for the synthesis of the iron complexes was prepared as follows: FeSO_4·7H_2O (277 mg, 1.00 mmol) and KSCN (194 mg, 2.00 mmol) were mixed in methanol (6 mL) and stirred for 30 min. Ascorbic acid (5 mg) was added to prevent oxidation. The solution was filtered over filter paper (to remove K_2SO_4) into a volumetric flask. The flask was filled up to 10 mL with methanol, resulting in a clear, colourless iron(II) solution, which must be used immediately. Filtration of the crude iron(II) compounds was done on Whatman membrane filters (regenerated cellulose) with 1 µm pores. ^1H NMR and ^13C NMR spectra were recorded at room temperature using a Bruker WM 300 MHz spectrometer. Chemical shifts are indicated in ppm relative to TMS. Infrared spectra were taken on a Perkin Elmer FT-IR Spectrometer Paragon 1000. Mass spectrometry was performed on a Finnigan Mat 900 spectrometer equipped with an electrospray interface. Elemental analysis was carried out on a Perkin-Elmer series II CHNS/O analyzer 2400.

2.5.2. Synthesis of R_2bapbpy ligands

**General procedure**: 6,6'-dibromo-2,2'-bipyridine (538 mg, 1.71 mmol), Pd(dbach) (21 mg, 0.036 mmol), (S)-BINAP (43 mg, 0.069 mmol) and KOrBu (770 mg, 6.86 mmol, 4 eq.) were added in a dry schlenk flask and put under argon. Dry, degassed toluene (10 mL) and the required α-aminopyridine (3 mmol) were added, and the mixture was heated to 80 °C and stirred under argon during 3 days. The suspension was cooled to room temperature and water (50 mL) was added. The mixture was stirred vigorously for 1 h. The solid was filtered and washed with water, diethyl ether and hexane. If necessary, the crude solid was purified by column chromatography on alumina (eluent CH_2Cl_2/MeOH mixtures) or reprecipitated from CH_2Cl_2/hexane, and finally dried under vacuum at 60 °C.

2: 2-amino-6-methylpyridine (324 mg, 3 mmol) was used. A crude white powder was obtained (141 mg, 26%). ^1H NMR (300 MHz, DMSO-^d_6): δ = 9.69 (s, 2H, H5), 7.89 (m, 2H, H4), 7.81 (d, J = 7.1 Hz, 4H, H3 + H7), 7.70 – 7.54 (m, 4H, H6 + H8), 6.78 (d, J = 7.3 Hz, 2H, H2), 2.42 (s, 6H, H1). ^13C NMR (300 MHz, DMSO-^d_6): 23.85(CH_3), 108.43(CH), 112.10(CH), 112.17(CH), 115.17(CH), 138.00(CH), 138.32(CH), 153.50(C), 153.61(C), 154.02(C), 155.89(C). ES-MS (DMF): m/z (calc): 369.14 (369.17, [M + H]^+). Elemental analysis calcd (%): for C_{22}H_{20}N_{6}: C 71.72, H 5.47, N 22.81; found: C 71.74, H 5.84, N 23.30. IR ν (cm^−1): 1593, 1558, 1564, 1516, 1456, 1436, 1361, 1322, 1263, 1238, 1148, 1090, 992, 872, 781, 733, 604, 546, 410, 317.
3: 2-amino-5-methylpyridine (324 mg, 3 mmol) was used. The resulting solid was purified by column chromatography (250 mL neutral alumina, DCM:MeOH, 95:5, R<sub>f</sub> = 0.4) to give a yellow powder (111 mg, 20%). H NMR (300 MHz, DMSO-<sup>d6</sup>): δ 9.65 (s, 2H, H5), 8.09 (s, 2H, H1), 7.90 (d, J = 8.5 Hz, 2H, H4), 7.87 – 7.67 (m, 4H, H4 + H6), 7.67 – 7.47 (m, 4H, H3 + H5), 2.23 (s, 6H, H2). 13C NMR (300 MHz, DMSO-<sup>d6</sup>): 17.21(CH<sub>3</sub>), 111.41(CH), 111.82(CH), 112.09(CH), 124.64(CH), 138.21(CH), 138.31(CH), 147.1(CH), 152.23(CH), 153.55(CH), 154.04(CH). ES-MS (DMF): m/z (calc): 369.34 (369.17, [M + H]<sup>+</sup>). Elemental analysis calcd (%) for C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>: C 71.72, H 5.47, N 22.81; found: C 69.21, H 5.70, N 23.03. IR ν (cm<sup>-1</sup>): 1652, 1576, 1558, 1520, 1506, 1428, 1386, 1300, 1145, 986, 802, 738, 632, 601, 560, 460, 411, 334, 328.

4: 2-amino-4-methylpyridine (324 mg, 3 mmol) was used to obtain a yellow powder (111 mg, 20%). H NMR (300 MHz, DMSO-<sup>d6</sup>): δ = 9.64 (s, 2H, H5), 8.10 (d, J = 5.0 Hz, 2H, H1), 7.81 (m, J = 3.9 Hz, 6H, H5 + H6 + H8), 7.65 (dd, J = 6.5, 2.4 Hz, 2H, H7), 6.74 (d, J = 4.7 Hz, 2H, H2), 2.31 (s, 6H, H3). 13C NMR (300 MHz, DMSO-<sup>d6</sup>): 21.35(CH<sub>3</sub>), 112.29(CH), 112.41(CH), 112.56(CH), 117.63(CH), 132.04(CH), 138.66(CH), 147.52(CH), 148.27(CH), 154.28(CH), 154.73(CH). ES-MS (DMF): m/z (calc): 369.14 (369.17, [M + H]<sup>+</sup>). Elemental analysis calcd (%) for C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>·H<sub>2</sub>O: C 68.38, H 5.74, N 21.75; found: C 68.85, H 5.59, N 21.11. IR ν (cm<sup>-1</sup>): 1612, 1576, 1563, 1558, 1520, 1506, 1428, 1386, 1300, 1150, 986, 778, 730, 668, 641, 523, 448, 316, 334.

5: 2-amino-3-picoline (324 mg, 3 mmol) was used to obtain a yellow powder (201 mg, 36%). H NMR (300 MHz, DMSO-<sup>d6</sup>): δ = 8.32 (s, 2H, H5), 8.13 (d, J = 4.7 Hz, 2H, H3), 7.94 (d, J = 8.1 Hz, H6), 7.87 (d, J = 7.4 Hz, H8), 7.79 (t, J = 7.8 Hz, H7), 7.57 (d, J = 7.3 Hz, H1), 6.92 (dd, J = 7.2, 5.0 Hz, 2H, H2), 2.33 (s, 6H, H4). 13C NMR (300 MHz, DMSO-<sup>d6</sup>): 21.35(CH<sub>3</sub>), 112.29(CH), 112.41(CH), 112.56(CH), 117.63(CH), 132.04(CH), 147.52(CH), 148.27(CH), 154.28(CH), 154.73(CH). ES-MS (DMF): m/z (calc): 369.50 (369.17, [M + H]<sup>+</sup>). Elemental analysis calcd (%) for C<sub>22</sub>H<sub>20</sub>N<sub>6</sub>: C 71.72, H 5.47, N 22.81; found: C 71.45, H 5.95, N 21.61. IR ν (cm<sup>-1</sup>): 1589, 1563, 1558, 1516, 1436, 1410, 1328, 1297, 1258, 1148, 1076, 988, 783, 755, 606, 531, 334, 324.
6: quinolin-2-amine (433 mg, 3 mmol) was used to give a yellow powder (295 mg, 45%). 

\[^1^H\text{NMR (300 MHz, DMSO-}\text{d}_6\text{): }\delta = 10.15\text{ (s, 2H, H7), 8.46 (dd, J = 7.5, 1.6 Hz, 2H, H8), 8.22 (dd, J = 8.9, 3.8 Hz, 2H, H6), 8.02 – 7.92 (m, 4H, H9 + H10), 7.80 (t, J = 8.9 Hz, 6H, H1 + H4 + H5), 7.69 – 7.61 (m, 2H, H2), 7.37 (dd, J = 10.9, 4.0 Hz, 2H, H3).}^1^C\text{NMR (300 MHz, DMSO-}\text{d}_6\text{): 112.70(CH), 113.52(CH), 114.29(CH), 123.38(CH), 124.12(C), 124.12(CH), 126.47(CH), 127.61(CH), 129.59(CH), 137.33(CH), 138.75(CH), 146.68(CH), 153.39(C), 153.45(C), 153.66(C).} \text{ES-MS (DMF): } m/z \text{ (calc): } 440.56 \text{ (440.17, [M + H]^+). Elemental analysis calcd (%) for C}_{28}\text{H}_{20}\text{N}_6\text{H}_2\text{O: C 73.35, H 4.84, N 18.33; found: C 73.33, H 4.54, N 17.96. IR } \nu \text{ (cm}^{-1}\text{): 1652, 1576, 1558, 1532, 1506, 1463, 1436, 1394, 1371, 1305, 1248, 1141, 1076, 992, 789, 754, 668, 632, 608, 567, 542, 472, 328, 306.}

7: isoquinolin-3-amine (250 mg, 1.73 mmol) was used. The resulting solid was purified by dissolving in a DCM solution and then adding hexane dropwise until precipitation occurred. The white solid was filtered and dried under vacuum at 60 °C (240 mg, 16%). 

\[^1^H\text{NMR (300 MHz, DMSO-}\text{d}_6\text{): }\delta = 10.01\text{ (s, 2H, H7), 9.15\text{ (s, 2H, H1), 8.81\text{ (s, 2H, H6), 8.03 (M, J = 8.4 Hz, 4H, H2 + H8), 7.96 (t, J = 7.7 Hz, 2H, H9), 7.86 (d, J = 8.2 Hz, 2H, H5), 7.69 (t, J = 7.6 Hz, 2H, H4), 7.45 (t, J = 7.5 Hz, 2H, H3), 7.37 (d, J = 8.0 Hz, 2H, H10).}^1^C\text{NMR (300 MHz, DMSO-}\text{d}_6\text{): 154.82(C), 151.672(CH), 150.18(C), 138.955(CH), 138.29(C), 138.207(C), 131.73(CH), 128.209(CH), 126.394(CH), 125.902(C), 124.687(CH), 112.981(CH), 112.609(CH), 103.919(CH).} \text{ES-MS (DMF): } m/z \text{ (calc): } 440.17 \text{ (440.17, [M + H]^+). Elemental analysis calcd (%) for C}_{28}\text{H}_{20}\text{N}_6\text{H}_2\text{O: C 70.57, H 5.08, N 17.64; found: C 71.70, H 4.47, N 17.30. IR } \nu \text{ (cm}^{-1}\text{): 1611, 1632, 1575, 1537, 1533, 1413, 1362, 1259, 1178, 1149, 986, 870, 783, 735, 686, 668, 638, 464.}

8: isoquinolin-1-amine (433 mg, 3 mmol) was used. The resulting solid was purified by dissolving the ligand in a DCM solution and then hexane was added dropwise until precipitation occurred. The yellow solid was filtered and dried it under vacuum at 60 °C (108 mg, 15%). 

\[^1^H\text{NMR (300 MHz, DMSO-}\text{d}_6\text{): }\delta = 9.64\text{ (s, 2H, H7), 8.64 (d, J = 8.5 Hz, 2H, H6), 8.29 (d, J = 8.2 Hz, 2H, H8), 8.10 (m, J =}
13.1, 6.6 Hz, 4H, H1 + H10 ), 7.97 – 7.85 (t, 4H, H3 + H9), 7.77 (t, J = 7.5 Hz, 2H, H4), 7.70 – 7.60 (t, 2H, H5), 7.36 (d, J = 5.7 Hz, 2H, H9). 13C NMR (300 MHz, DMSO-d6): 153.72(C), 153.47(C), 151.77(C), 140.32(CH), 138.12(CH), 136.93(C), 130.36(CH), 126.80(CH), 126.59(CH), 123.89(CH), 119.04(C), 114.30(CH), 114.21(CH), 113.96(CH). ES-MS (DMF): m/z (calc): 440.10 (440.17, [M + H]+). Elemental analysis calcd (%) for C28H20N6·H2O: C 73.35, H 4.84, N 18.33; found: C 73.19, H 4.54, N 17.96. IR ν (cm⁻¹): 1652, 1588, 1558, 1494, 1436, 1330, 1240, 1270, 1240, 1165, 988, 834, 786, 638, 516, 468, 386, 344.

2.5.3. Synthesis of the iron complexes

**General procedure:** In a round bottom flask the suitable ligand (0.15 mmol), [Fe(NCS)2] (1.6 mL of a 0.1 M methanolic solution, 1.1 eq.) and ascorbic acid (5 mg) were added. The flask was closed and the suspension was stirred overnight. The solid was collected by filtration over a micropore filter, thoroughly washed with methanol, and dried under vacuum.

**Crystal growing:** Single crystals suitable for X-ray diffraction study were obtained for compounds 11, 12 and 15 as follows: the crude powder (50 mg) was dissolved in dry, degassed DMF (10 mL), affording a dark solution which became red after addition of a small amount of ascorbic acid (5 mg). Aliquots (1 mL) of this solution were put into 10 reaction tubes. Degassed methanol was layered on top of these samples, and the 10 tubes were stoppered and left untouched. Dark crystals were obtained within a few days by liquid-liquid diffusion. The crystals were collected, washed with MeOH, and dried under vacuum. For compound 10: ligand 3 (20 mg) was dissolved in degassed DMF (4 mL). 1 mL aliquots of this solution were pipette-filtered over 1 cm Celite into five Corning tubes. To each tube 0.22 mL of the Fe(NCS)2 solution was carefully added to create a two-layer system. Degassed methanol was then layered on top of these layers. The tubes were then stoppered and left untouched at room temperature, and if possible under sunlight, to allow slow liquid/liquid diffusion. Within 3 days, red crystals of 10 appeared at the wall of the vials. The tubes were immediately sent for single crystal X-ray structure determination.

9: The yellow compound was obtained with a yield of 77%. IR ν (cm⁻¹): 3344, 2056 (NCS⁻), 1636, 1606, 1590, 1534, 1418, 1456, 1436, 1224, 1174, 1000, 779, 753, 739, 697, 643, 514, 482, 324, 318. 1H NMR (300 MHz, DMSO-d6): δ = 9.69 (s, 2H), 7.89 (d, J = 7.8 Hz, 2H), 7.82 (s, 4H), 7.71 – 7.49 (m, 4H), 6.77 (d, J = 6.6 Hz, 2H), 2.41 (s, 6H). HR-MS (DMF): m/z (calc): 482.0856 (482.0845, [M – NCS]⁺).
The orange compound was obtained with a yield of 76%. IR ν (cm⁻¹): 3294, 2093 (NCS⁻), 2061 (NCS⁻), 1627, 1616, 1582, 1531, 1496, 1461, 1440, 1436, 1237, 1177, 1048, 1012, 820, 792, 636, 638, 512, 430, 322. ¹H NMR (300 MHz, DMSO-d⁶): δ = 78.34, 66.75, 58.73, 44.28, 23.37, 8.01, 7.83, 7.58, 7.55, 6.61. ES-MS (DMF): m/z (calc): 482.26 (482.09, [M − NCS]⁺). Crystal data (at 110(2) K): Fw = 540.45, orange red irregular needle, 0.44 × 0.15 × 0.08 mm³, triclinic, P-1 (no. 2), a = 8.5705(3), b = 10.9724(4), c = 13.3111(4) Å, α = 69.364(3), β = 79.591(3), γ = 80.737(3)°, V = 1145.71(7) Å³, Z = 2, Dₓ = 1.567 g cm⁻³, μ = 0.873 mm⁻¹, abs. corr. range: 0.758–0.952. 13952 Reflections were measured up to a resolution of (sin θ/λ)max = 0.62 Å⁻¹. 4624 Reflections were unique (Rint = 0.0513), of which 4034 were observed [I > 2σ(I)]. 326 Parameters were refined using 2 restraints. R1/wR2 [I > 2σ(I)]: 0.0301/0.0770. R1/wR2 [all refl.]: 0.0364/0.0798. S = 1.030. Residual electron density found between −0.30 and 0.37 e Å⁻³.

The rusty compound was obtained with a yield of 91%. Single crystals were obtained by liquid-liquid diffusion from MeOH into DMF. IR ν (cm⁻¹): 2853, 2923, 2362, 2075 (NCS⁻), 1634, 1533, 1490, 1236, 1174, 1010, 790, 643, 449, 330, 325. ¹H NMR (300 MHz, DMSO-d⁶): δ = 77.04, 67.63, 58.35, 44.35, 27.64, 24.26, 15.78, 9.68, 8.13, 7.84, 7.68, 6.77. ES-MS (DMF): m/z (calc): 481.86 (482.09, [M − NCS]⁺). Crystal data (at 110(2) K): Fw = 540.45, orange irregular plate, 0.34 × 0.24 × 0.07 mm³, monoclinic, C2/c (no. 15), a = 15.7947(6), b = 12.1802(2), c = 14.5597(5) Å, β = 122.729(5)°, V = 2356.33(18) Å³, Z = 4, Dₓ = 1.523 g cm⁻³, μ = 0.849 mm⁻¹, abs. corr. range: 0.832–0.950. 8245 Reflections were measured up to a resolution of (sin θ/λ)max = 0.65 Å⁻¹. 2684 Reflections were unique (Rint = 0.0452), of which 2210 were observed [I > 2σ(I)]. 164 Parameters were refined with 1 restraint. R1/wR2 [I > 2σ(I)]: 0.0343/0.0892. R1/wR2 [all refl.]: 0.0436/0.0913. S = 1.036. Residual electron density found between −0.32 and 0.33 e Å⁻³.

The rusty compound was obtained with a yield of 91%. Dark red single crystals were obtained by liquid-liquid diffusion from MeOH into DMF in 29% yield. IR ν (cm⁻¹): 3392, 2363, 2063 (NCS⁻), 1620, 1587, 1530, 1469, 1436, 1229, 1174, 1005, 788, 648, 580, 325. ¹H NMR (300 MHz, DMSO-d⁶): δ = 72.08, 58.24, 43.39, 30.04, 27.18, 19.07, 8.32, 8.13, 7.87, 7.79, 7.57, 6.92, 2.33. ES-MS (DMF): m/z (calc): 481.88 (482.09, [M − NCS]⁺). Elemental analysis calcd (%) for C24H20FeN8S2: C 53.34, H 3.73, N 20.73; found: C 52.98, H 3.98, N 20.68. Crystal data: Phase I (at 295 K): Fw = 540.45, dark red diamond, 0.64 × 0.24 × 0.20 mm³, monoclinic, C2/c (no. 15), a = 13.2932(3), b = 13.2099(2), c = 14.3032(3) Å, β = 103.715(2)°, V = 2440.05(8) Å³, Z = 4, Dₓ = 1.471 g cm⁻³, μ = 0.820 mm⁻¹, abs. corr. range: 0.710–0.874. 9143 Reflections were measured up to a resolution of (sin θ/λ)max =
0.606 Å\(^{-1}\). 2280 Reflections were unique (\(R_{int} = 0.0190\)), of which 2020 were observed \([I > 2\sigma(I)]\). 164 Parameters were refined with 1 restraint. \(R1/wR2 [I > 2\sigma(I)]: 0.0269/0.0735.\) \(R1/wR2 [all \text{ refl.}]: 0.0311/0.0755.\) S = 1.074. Residual electron density found between –0.30 and 0.23 e Å\(^{-3}\). \textbf{Phase II} (at 110 K): \(Fw = 540.45,\) dark red diamond, 0.64 × 0.23 × 0.22 mm\(^3\), monoclinic, \(C2/c\) (no. 15), \(a = 13.1548(2), b = 13.21019(18), c = 14.1638(2) Å, β = 107.2514(16)°, V = 2350.62(6) Å\(^3\), \(Z = 4, D_x = 1.527 \text{ g cm}^{-3}, \mu = 0.851 \text{ mm}^{-1}, \text{ abs. corr. range: 0.697–0.868.}\) 12820 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ Å}^{-1}\). 2694 Reflections were unique (\(R_{int} = 0.0447\)), of which 2493 were observed \([I > 2\sigma(I)]\). 164 Parameters were refined with 1 restraint. \(R1/wR2 [I > 2\sigma(I)]: 0.0295/0.0821.\) \(R1/wR2 [all \text{ refl.}]: 0.0314/0.0833.\) S = 1.078. Residual electron density found between –0.54 and 0.45 e Å\(^{-3}\).

\textbf{13:} The orange complex was obtained with a yield of 61%. IR \(\nu\) (cm\(^{-1}\))): 3080, 2362, 2036 (NCS\(^{-}\)), 1652, 1584, 1563, 1532, 1461, 1294, 1242, 794, 751, 473. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 10.16\) (s, 2H), 8.47 (d, \(J = 5.6\) Hz, 2H), 8.24 (d, \(J = 8.3\) Hz, 2H), 8.00 (s, 4H), 7.82 (t, \(J = 8.1\) Hz, 6H), 7.71 – 7.60 (m, 2H), 7.41 (d, \(J = 6.4\) Hz, 2H). HR-MS (DMF): \(m/z\) (calc): 554.0838 (554.0845, [M – NCS]\(^+\)).

\textbf{14:} The red complex was obtained with a yield of 92%. IR \(\nu\) (cm\(^{-1}\))): 3294, 2062 (NCS\(^{-}\)), 1636, 1616, 1576, 1564, 1541, 1490, 1474, 1404, 1322, 1247, 1171, 1004, 866, 786, 664, 635, 459, 425. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 10.01\) (s, 2H), 9.15 (s, 2H), 8.81 (s, 2H), 8.03 (M, \(J = 8.4\) Hz, 4H), 7.96 (t, \(J = 7.7\) Hz, 2H), 7.86 (d, \(J = 8.2\) Hz, 2H), 7.69 (t, \(J = 7.6\) Hz, 2H), 7.45 (t, \(J = 7.5\) Hz, 2H), 7.37 (d, \(J = 8.0\) Hz, 2H). ES-MS (DMF): \(m/z\) (calc): 554.06 (554.08, [M – NCS]\(^+\)).

\textbf{15:} The brown compound was obtained with yield of 81%. Dark brown single crystals were obtained by liquid-liquid diffusion from MeOH into DMF in 32% yield. IR \(\nu\) (cm\(^{-1}\))): 2365, 2110 (NCS\(^{-}\)), 2071 (NCS\(^{-}\)), 1636, 1610, 1593, 1532, 1506, 1436, 1233, 796, 740, 668, 664, 581, 477. \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 72.92, 73.50, 28.19, 26.37, 25.66, 22.49, 10.47, 9.31, 8.64, 8.26, 8.10, 8.06, 7.91, 7.77, 7.66, 7.36.\) ES-MS (DMF): \(m/z\) (calc): 554.04 (554.08, [M – NCS]\(^+\)).

Crystal data: \textbf{Phase I} (at 300 K): \(Fw = 612.51,\) dark brown block, 0.39 × 0.24 × 0.09 mm\(^3\), monoclinic, \(C2/c\) (no. 15), \(a = 13.1139(3), b = 13.9825(3), c = 14.8988(4) Å, \beta = 92.719(2)°, V = 2728.84(11) Å\(^3\), \(Z = 4, D_x = 1.491 \text{ g cm}^{-3}, \mu = 0.743 \text{ mm}^{-1}, \text{ abs. corr. range: 0.794–0.933.}\) 8264 Reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.59 \text{ Å}^{-1}\). 2413 Reflections were unique (\(R_{int} = 0.0235\)), of which 2070 were observed \([I > 2\sigma(I)]\). 190 Parameters were refined with 1 restraint. \(R1/wR2 [I > 2\sigma(I)]: 0.0347/0.0952.\) \(R1/wR2 [all \text{ refl.}]: 0.0314/0.0833.\) S = 1.078. Residual electron density found between –0.54 and 0.45 e Å\(^{-3}\).
refl.]: 0.0410/0.0974. S = 1.094. Residual electron density found between –0.40 and 0.58 e Å⁻³. **Phase II** (at 110 K): Fw = 612.51, dark brown block, 0.38 × 0.28 × 0.11 mm³, monoclinic, C2/c (no. 15), a = 12.9785(2), b = 13.9262(3), c = 14.5637(3) Å, β = 93.7103(17)°, V = 2626.74(9) Å³, Z = 4, Dₓ = 1.549 g cm⁻³, μ = 0.772 mm⁻¹, abs. corr. range: 0.795–0.927. 8254 Reflections were measured up to a resolution of (sin θ/λ)max = 0.62 Å⁻¹. 2579 Reflections were unique (Rint = 0.0251), of which 2224 were observed [I > 2σ(I)]. 190 Parameters were refined with 1 restraint. R1/wR2 [I > 2σ(I)]: 0.0290/0.0748. R1/wR2 [all refl.]: 0.0352/0.0765. S = 1.034. Residual electron density found between –0.46 and 0.44 e Å⁻³.

**X-Ray diffraction studies:** All reflection intensities were measured using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.33.55, Oxford Diffraction Ltd., 2010). The program CrysAlisPro was used to refine the cell dimensions. Data reductions were done using the program CrysAlisPro. The structures were solved with the program SHELXS-97 and were refined on F² with SHELXL-97.³⁵ Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro. The temperatures of the data collections were controlled using the system Cryojet (manufactured by Oxford Instruments). The H-atoms were placed at calculated positions (except for that located on N2) using the instructions AFIX 43, or AFIX 137 (only for 11 and 12) with isotropic displacement parameters having values 1.2 or 1.5 times Ueq of the attached C atoms. The positions and the isotropic temperature factors of the H atoms located on N2 (i.e., H2A) were refined freely. The distances N2–H2A were restrained to be 0.83(3) Å.

**Magnetic susceptibility** data were measured on a Quantum Design MPMS-XL squid magnetometer from powder samples for compounds 9, 10, 13 and 14, and from recrystallized samples for compounds 11, 12, and 15. In all cases, the ~10-20 mg sample was inserted in a plastic straw before introduction in the magnetometer. DC magnetization measurements were performed in a field of 0.5 T, from 300 to 3 K (cooling mode) and from 3 to 300 K (heating mode) with a rate of 0.3–1.1 K min⁻¹ for compounds 9-14, and from 80 to 400 K (heating mode) and from 400 to 80 K (cooling mode) with a rate of 0.3–1.1 K min⁻¹ for compound 15. The total measuring time was 20 h. The transition temperatures were obtained using the first derivative of χMT = f(T). Corrections for the diamagnetism of the sample were calculated using Pascal’s constants.³⁶

**Differential Scanning Calorimetry** (DSC): Heat capacities were obtained by use of a differential scanning calorimeter Q1000 with the LNCS accessory from TA Instruments.
The temperature and enthalpy scales were calibrated with a standard sample of indium, using its melting transition (156.6 °C, 3296 J mol\(^{-1}\)). The measurements were carried out using 6 to 13 mg of samples sealed in aluminum pans with mechanical crimp, with an empty pan as reference. The zero-heat flow procedure described by TA Instruments was followed, using as reference compound a synthetic sapphire. Using this procedure, an overall accuracy of ca. 0.2 K in temperature and up to 5 to 10% in the heat capacity is estimated over the whole temperature range.

**Optical microscopy**: Optical microscopy images of single crystals of 1 and 12 were recorded in bright-field transmission mode using an Olympus BX51 microscope equipped with a 640×512 colour camera (Moticam), a halogen lamp (400-700 nm) and a 50× long-working-distance objective (NA=0.5). The sample was enclosed in a Linkam THMS600 liquid nitrogen cryostat equipped with glass windows. The heating and cooling rates were 5 K min\(^{-1}\) and images were taken every 30 s.

### 2.6. References: