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**Title:** Mononuclear spin-transition materials based on the bapbpy scaffold  
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Conclusions and outlook
8.1 Ligand modifications and new spin-crossover materials

Cooperative spin-crossover Fe(II) compounds showing thermal hysteresis exhibit magnetic and colourmetric bistability, which is of interest for a number of applications such as information storage and optical displays.¹ Mononuclear iron(II) complexes hold considerable potential in this field, and their properties may suffer less from size reduction effects than polymeric SCO materials because the coordination environment remains well defined throughout the material. However, the ideal mononuclear SCO complex is still rare as a high transition temperature and high cooperativity require strong ligands for Fe(II) and strong intermolecular interactions. One of the goals of this project was to design new mononuclear Fe(II) compounds based on the bapbpy ligand, i.e., derivatives of the highly cooperative SCO compound $[\text{Fe(bapbpy)}(\text{NCS})_2]$ (1),² with higher transition temperatures. Four Chapters of this thesis focus hence on increasing the transition temperature of 1 while maintaining a hysteresis cycle (see Chapters 2, 4, 5 and 6, and Table 8.1).

The ligand bapbpy is a rigid, embracing N₄ ligand leaving two *trans* positions on the coordination sphere for coordination of axial ligands.² By adding electron-donating methyl groups on the four different positions of the terminal pyridine rings, only one SCO compound $[\text{Fe(Me₂bapbpy)}(\text{NCS})_2]$ was obtained (Chapter 2, 2, see Table 8.1). However, its transition temperature is low (170 K) and the compound shows no hysteresis cycle. On the other hand, when more conjugated quinoline or isoquinoline substituents were used instead of the terminal pyridine rings, two new SCO compounds were obtained. One remains cooperative as in 1 (i.e., with hysteresis cycle), but has a low transition temperature (3, Table 8.1); the other one shows a promising near room-temperature transition (288 K, 4 in Table 8.1), but no hysteresis cycle. The X-ray crystallography data of SCO compounds 2 and 4 show similar crystal packing, which features N–H···S hydrogen-bond networks. However, because of the substituents at the β, β’ positions on the terminal pyridine rings (Figure 8.1), these N–H···S intermolecular interactions are weaker compared to those in compound 1. Overall, for bapbpy-based SCO compounds the strength of these N–H···S hydrogen bonds correlates well with the cooperativity of the spin transition, and it appears to be important to keep the β positions on the bapbpy ligand vacant in order to maintain cooperativity. Strikingly, different isomers of the same mononuclear iron(II) complex give materials of very different SCO properties. Overall, by modifying the chemical structure of the bapbpy
ligand the transition temperature of the SCO compounds was increased to near room
temperature, but unfortunately at the cost of cooperativity.

![Figure 8.1. General schematic drawing of the iron(II) SCO complexes studied in this thesis based on the bapbpy ligand. X=S or Se.](image)

Because minor chemical changes on the bapbpy ligand led to significant changes in the
SCO properties of its Fe(II) compound, another approach was tried, which consisted in
replacing the axial NCS$^-$ ligand by more electron donating NCSe$^-$ ligands (Chapter 4). Five new iron(II) SCO compounds 5-9 (Table 8.1) were obtained with the same R$_2$bapbpy derivatives as described in Chapter 2. Two were found to be cooperative SCO materials (6 and 8), whereas the others showed non-cooperative SCO. For 6 and 8, although the transition temperatures are still far lower than room temperature, a trend was observed: their transition temperature is increased compared to the NCS$^-$ analogues. In particular, compound 6 does show SCO whereas its thiocyanate analogue does not. Consistently, for the non-cooperative SCO compounds 7 and 9, the same trend was also observed, with the transition temperature of 9 (357 K) being the highest of all bapbpy-based compounds reported to date. By comparing the X-ray structures of compounds 7 and 9 with those of 2 and 4, a striking structural similarity was found between the thiocyanate and selenocyanate compounds, indicating that the increase of the transition temperature has a purely electronic origin. Compound 5 appears to be an exception, as its dramatically lower cooperativity compared to compound 1 seems to be the result of a change in X-ray structure of the Fe(II) compound when going from NCS$^-$ to NCSe$^-$ axial ligands, rather than an electronic effect.

By using a phenanthroline backbone instead of a bipyridine, not only the rigidity of the
ligand is increased, but also the ligand field strength, since phen is a stronger ligand
than bpy in the spectrochemical series (Chapter 5). Two new iron(II) SCO compounds
were obtained with the new bapphen ligand (10 and 11, Table 8.1). Interestingly,
different forms exist for compound 10, which are obtained by different preparation methods. The first form could not be crystallized but shows a three-step, incomplete SCO with a hysteresis cycle just below room temperature (280 K), whereas the second form crystallizes more easily but has no SCO properties. In compound 11, in which the NCS\(^{-}\) ligands were replaced with NCSe\(^{-}\) ligands, the cooperativity was lost, similar to what was observed for the bapbpy complexes (e.g., 5 vs. 1).

Finally, the most promising SCO compound described in this thesis, [Fe(bbpya)(NCS)\(_2\)] (12, Table 8.1), was designed by a very different approach consisting in replacing one of the 6-membered rings found in bapbpy-based metal complexes, by a 5-membered ring (Chapter 6). The new ligand bbpya is a rigid and almost flat ligand in which two bipyridines are connected by a single amine bridge. Its iron(II) complex 12 indeed shows a decreased distortion of the octahedral coordination environment compared to 1. As a result, 12 is low-spin (LS) at room temperature in the solid state and shows one of the highest transition temperatures recorded among known mononuclear SCO complexes. Most interestingly, it keeps a large hysteresis cycle of 21 K although each bbpya ligand has only one NH bridge to build hydrogen bonding networks. Crystal data revealed that cooperativity is maintained due to the disorder in the structure, which results in infinite supramolecular chains via hydrogen-bonding and π-π stacking interactions. Overall, the uncommon features of 12 validate the strategy of replacing 6-membered chelate rings by 5-membered ones to increase the transition temperature.

**Figure 8.2.** Summary of χ\(_{MT}\) vs. \(T\) curves for all SCO compounds 1-13 described in this thesis. The number codes are referred to Table 8.1 (see next page).
Table 8.1. Summary of transition temperatures ($T_{1/2}$), hysteresis widths ($\Delta T_{\text{hyst}}$) and the number $n$ of like-spin SCO centres per interacting domain of all new SCO compounds $[\text{Fe}(L)(\text{NCX})_2]$ described in this thesis (2-13) and, for comparison, of the reference compound $[\text{Fe}(\text{bapbpy})(\text{NCS})_2]$ (1).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Chapter</th>
<th>Ligand L</th>
<th>NCX</th>
<th>$T_{1/2}$ (K)$^a$</th>
<th>$\Delta T_{\text{hyst}}$ (K)</th>
<th>$n$</th>
<th>Special observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−</td>
<td>bapbpy</td>
<td>NCS</td>
<td>235↓ / 239↑$^{(1\text{st})}$ / 172↓ / 194↑$^{(2\text{nd})}$</td>
<td>4 / 22</td>
<td>11.6 / 22.5</td>
<td>2-step SCO, with distinctive IP</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$\beta,\beta'$-Me$_2$bapbpy</td>
<td>NCS</td>
<td>170(2)</td>
<td>–</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>R$_2$bapbpy$^b$</td>
<td>NCS</td>
<td>113(2)↓ / 125(2)↑</td>
<td>11(3)</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>R$_2'$bapbpy$^c$</td>
<td>NCS</td>
<td>288(5)</td>
<td>–</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>bapbpy</td>
<td>NCS</td>
<td>195(4)</td>
<td>–</td>
<td>5.8</td>
<td>Gradual transition</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>$\delta,\delta'$-Me$_2$bapbpy</td>
<td>NCS</td>
<td>113(4)↓ / 137(4)↑</td>
<td>24(6)</td>
<td>14.4</td>
<td>Replace NCS by NCSe leads to SCO</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>$\beta,\beta'$-Me$_2$bapbpy</td>
<td>NCS</td>
<td>214(20)</td>
<td>–</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>R$_2$bapbpy$^b$</td>
<td>NCS</td>
<td>141(4)↓ / 149(4)↑</td>
<td>8(6)</td>
<td>54.8 / 70.5</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>R$_2'$bapbpy$^c$</td>
<td>NCS</td>
<td>357(19)</td>
<td>–</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>bapphen$^d$</td>
<td>NCS</td>
<td>268(4)↓ / 280(4)↑$^e$</td>
<td>12(6)</td>
<td>2 forms, one showing multi-step transition</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>bapphen</td>
<td>NCS</td>
<td>101(4)</td>
<td>–</td>
<td>Gradual transition</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>6</td>
<td>bbpya</td>
<td>NCS</td>
<td>407(3)↓ / 428(1)↑</td>
<td>21(3)</td>
<td>10.2 / 6.5</td>
<td>LS at RT</td>
</tr>
<tr>
<td>13</td>
<td>7</td>
<td>bapphen-C$_{12}$</td>
<td>NCS</td>
<td>182(25)</td>
<td>–</td>
<td>Gradual transition, self assembly on HOPG$^f$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $T_{1/2}$ values were obtained based on magnetic susceptibility measurements on samples prepared by method $a$, ↓ and ↑ indicate $T_{1/2}$ in cooling and in the heating mode respectively, the errors are also given in the brackets. $^b$ R$_2$bapbpy contains isoquin-3-oline substituents. $^c$ R$_2'$bapbpy contains isoquin-1-oline substituents. $^d$ Transition temperatures are given based on the SCO form of $[\text{Fe}(\text{bapphen})(\text{NCS})_2]$. $^e$ Only the transition temperatures for the hysteresis (first-step transition) are given.
8.2 Understanding the cooperativity in [Fe(bapbpy)(NCS)$_2$]

In the research described in this thesis, the cooperativity of the SCO of [Fe(bapbpy)(NCS)$_2$] (1) was studied by diluting the iron complex with increasing amounts of its magnetically inert Zn(II) analogue (Chapter 3). The initial idea was to investigate to which extent the two-step SCO and hysteresis cycles remain when the average Fe–Fe distance becomes larger. However, the zinc analogue of 1 shows a different crystallographic structure compared to 1, due to the different geometric preferences of the Zn(II) ion. Single crystals of cocrystallized [Fe$_x$Zn$_{1-x}$(bapbpy)(NCS)$_2$] could not be obtained, as a result of which the study of the diluted compounds was completed using powder samples. Based on powder X-ray diffraction, magnetic susceptibility measurements, and infrared spectroscopy data, it appeared that in the zinc-diluted samples containing a majority of iron ($x > 0.53$) the phase of the iron compound was retained. At higher dilutions, the phase of the zinc analogue gradually took over, but the SCO of the iron compound remained observable at an iron fraction as low as $x = 0.24$. Upon decreasing the iron fraction $x$ the two hysteresis cycles initially became narrower, and then vanished at $x = 0.76$, to lead to a single-step SCO material with some degree of cooperativity. Further increasing the zinc content led to the gradual loss of the cooperativity and to a fully non-cooperative SCO material at the lowest iron fraction studied ($x = 0.24$). Overall, this study clearly shows that the two steps and the hysteresis cycles of the SCO are two consequences of the same phenomenon: intermolecular interactions between spin-switching molecules. These two different manifestations of cooperativity are both lost simultaneously upon dilution.

8.3 SCO material on a surface

For nanomemory applications, the major goal is to perform spin switching of a single molecule at a surface. The current challenge includes controlling the self-organization and addressability of SCO molecules at surfaces. In this thesis, a new bapphen-based ligand bearing a 12-carbon chain at the back of the tetrapyridyl ligand is described. Although such functionalization represents extensive modifications of the polypyridyl ligand, the iron complex 13 (Table 8.1) still shows spin transition in the bulk material, although it is gradual and does not show a hysteresis cycle. The long alkyl chain helps the complex to self-assemble on a highly oriented pyrolytic graphite (HOPG) surface, where the molecules appear to form stable and highly ordered 2D patterns. The
periodicity of these patterns as observed by STM is different from the periodicity of similar patterns made by the free ligand on HOPG. A model was built that suggests that the N−H⋯S intermolecular interactions still exist at the HOPG surface for the iron complex 13. This in turn suggests that molecules of 13 might show cooperative SCO once deposited on HOPG. Variable temperature STM is not a straightforward technique though, and collaboration on this topic is currently ongoing with the group of Atomic and Molecular Conductors (AMC) at the Leiden Institute of Physics. Overall, the introduction of long alkyl chains on the bapphen ligand without blocking the N−H bridges appears to be a valid strategy to deposit and organise SCO molecules onto surfaces.

8.4 Outlook and future perspectives

One of the major goals in the field of spin crossover is to “rationally design” mononuclear SCO compounds with high transition temperature and high cooperativity. “Rational design” involves understanding of the SCO phenomenon and being able to predict the properties of a given compound. This goal was pursued by making use of the ligand-field theory (see Chapter 1). Many different ligands were investigated for their abilities to increase the ligand field strength around the Fe(II) ion, to increase the transition temperature of the SCO of their iron complexes. Regarding cooperativity a model was built that predicts cooperative SCO when the N−H⋯S hydrogen bonds are strong, i.e., when there is no substituent hampering hydrogen-bond interactons and when the intermolecular N⋯S distances are short (~3.4 Å), whereas non-cooperative SCO occurs when a substituent weakens the N−H⋯S hydrogen bonds by elongating the intermolecular N⋯S distances (3.9 to 4.1 Å). We are able to show that indeed mononuclear SCO compounds with high transition temperature and high cooperativity can be obtained.

However, it was found that extreme small changes, for example, replacing the S atom of the NCS anion with less electronegative Se atom in NCSe, represents a modification that is important enough to radically change the SCO properties of the complex. This extreme sensitivity of SCO to minute changes of the compound culminates in sample preparation, where the same compound prepared with different methods gives different forms with different SCO properties. The mere occurrence of SCO, as well as the transition temperatures, are still impossible to link in a straightforward manner to the
ligand field strength, as other parameters such as packing effects play a critical role in the magnetic properties of these SCO compounds.

For the high-temperature, cooperative SCO compound [Fe(bbpya)(NCS)₂] (12, Table 8.1), the strategy of decreasing the distortion of the octahedral coordination environment was a very successful approach. A high cooperativity remains even with only one NH bridge presents per complex, which could open a new door for the design of new rigid N₄ ligands. In practice indeed, the transition temperature of this compound may even be too high for information storage applications. Transition temperatures situated around 298 K are preferred, which may be obtained by replacing the axial NCS⁻ ligands in this compound by the less electron-donating NCO⁻ ligands. However, the high transition temperature of compound 12 allows for studying mechanistic and microscopic aspects of cooperative SCO that are more difficult to study in a cooled environment. Collaboration in this direction has been started with the group of Azzedine Bousseksou and Gabor Molnar in Toulouse.

It is worth mentioning that many SCO compounds described in this thesis have relatively low molecular weights, are neutral, and do not contain any solvent molecules in the crystal lattice. Therefore, they are in principle suitable for evaporation under ultra-high vacuum conditions to obtain clean, well-organized monolayers or sub-monolayers on surfaces. The transition temperatures of these compounds in the bulk are ranging from 113 K to 428 K. Thus, if it were possible to vary the temperature of an STM setup, it might be possible to observe whether SCO occurs for these complexes, either at the single-molecule level or at the level of a cluster of a few molecules, and to check whether such small clusters show cooperative SCO properties or not.

The initial results of compound 13 self-assembled on HOPG by dip coating are very promising, as this compound seems to form infinite 1D chains connected via the alkyl tails into large 2D domains. However, for practical applications both the transition temperature and synthetic availability of such compounds have to be improved. One of the reasons for the low transition temperature and high residual HS fraction at low temperature for this compound is most likely due to the extensive modification of the organic backbone of the bapphen ligand. It might be interesting to attach two alkyl chains at the 5,6 positions on the bapphen ligand, as shown in Figure 8.3. Such a ligand
potentially would be significantly easier to prepare than the ligand used in compound 13.

![Figure 8.3. Proposed synthetic route towards a two-tailed baphen-based iron(II) compound.](image)

Even with compounds showing high cooperativity in the bulk, it is not guaranteed that the SCO molecules would remain cooperative on surfaces. The SCO will indeed depend on substrate-molecule interactions as well. It would be interesting to immobilize compound 13 onto a self-assembled monolayer (SAM) of alkanethiols on a gold surface (Figure 8.4). By doing so, the molecules are expected to hold roughly perpendicularly to the surface due to supramolecular interactions (van der Waals force). It is thus conceivable that hydrogen bonding and π–π stacking interactions may occur in such a system, thereby allowing cooperativity. Another advantage of using SAMs on gold surfaces is that defects and pollutants on the surface may be readily displaced by the thiols. This may lead to very flat surfaces, which would help the detection and characterization of the SCO molecules by STM. Overall, the question of the minimal size at which 2D clusters of SCO molecules show cooperative behaviour, is not resolved yet.
Figure 8.4. Immobilizing molecules of compound 13 to a self-assembled monolayer of alkanethiols on a gold surface.

8.5 References: