Fe(Me2-bpy)2(NCSe)2 spin-crossover micro- and nanoparticles showing a spin-state switching above 250 K.

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**Supplementary Materials**

**Table ST1:** Crystal data and structure refinement for [Fe(Me2-bpy)3](NCSe)2 . 3(H2O) at 100 K.

**Table ST2:** Geometry of the Fe site surroundings in [Fe(Me2-bpy)3](NCSe)2 . 3(H2O)

**Table ST3:** Raman data characterizing [Fe(Me2-bpy)3](NCSe)2.3H2O (200 K) and Fe(Me2-bpy)2(NCSe)2 (370 and 200 K, in the HS and LS state respectively)

**Video** showing the thermal evolution of both type of crystals: [Fe(Me2-bpy)3](NCSe)2 . S (S = CH₃OH or H₂O).

**Figure S1:** Evolution of the crystal edges size and angle determined from optical microscopy images at 160 °C.

**Figure S2:** IR spectra of the powder of precursor recorded at 293 K before and after the thermal reaction. Inset: expansion showing the frequency range of νNC.

**Figure S3:** TEM images showing the 460 and 56 nm particles, that as described in the text, simultaneously precipitate by sudden addition of the ethanolic solution of precursor in toluene.

**Figure S4:** Superimposition of the temperature dependence of χMT reported for Fe(Me2bpy)2(NCSe)2.H2O in reference 8 and the one of the compound here prepared by thermal treatment of [Fe(Me2bpy)3](NCSe)2 . 3H2O.

**Figure S5:** Raman spectra recorded for [Fe(Me2-bpy)3](NCSe)2.3H2O before (left) and after (right) thermal treatment.

**Figure S6:** Raman spectra of nanoparticles of Fe(Me2-bpy)2(NCSe)2 recorded at different temperatures (a) 1.2 μm microparticles, (b) 460 nm nanoparticles; (c) 56 nm nanoparticles.

**Figure S7:** Comparison between the variation of relative intensity of the LS peak from Raman measurements (▲bulk, ●1.2 μm, ◆460 nm, ◆56 nm) and the HS fraction curves determined from magnetic measurements (dashed lines with the related colors)
Table ST1: Crystal data and structure refinement for [Fe(Me₂-bpy)₃][NCSe]₂ · 3(H₂O) at 100 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C₃₈H₃₆Fe₈N₈O₃Se₂</td>
</tr>
<tr>
<td>Formula weight</td>
<td>866.52</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100 (1)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71069</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.203(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>19.513(2)</td>
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<tr>
<td>c (Å)</td>
<td>15.887(1)</td>
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<tr>
<td>α (°)</td>
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<tr>
<td>β (°)</td>
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<tr>
<td>γ (°)</td>
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<tr>
<td>V (Å³)</td>
<td>3782.5(6)</td>
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<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calc.) (g.cm⁻³)</td>
<td>1.521</td>
</tr>
<tr>
<td>Abs. coefficient (mm⁻¹)</td>
<td>2.371</td>
</tr>
<tr>
<td>F(000)</td>
<td>1752</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.27 × 0.18 × 0.04</td>
</tr>
<tr>
<td>θ range (°)</td>
<td>1.65 → 30.54</td>
</tr>
<tr>
<td>h</td>
<td>-17 → 14</td>
</tr>
<tr>
<td>k</td>
<td>-27 → 27</td>
</tr>
<tr>
<td>l</td>
<td>-22 → 22</td>
</tr>
<tr>
<td>No. of reflections collected</td>
<td>58258</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>11051</td>
</tr>
<tr>
<td>Rint</td>
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</tr>
<tr>
<td>Data[I &gt; 2σ(I)] / restraints / parameters</td>
<td>7492 / 58 / 502</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>R1 [I &gt; 2σ(I)]</td>
<td>0.0464</td>
</tr>
<tr>
<td>wR2 [I &gt; 2σ(I)]</td>
<td>0.1128</td>
</tr>
<tr>
<td>R1 (all data)</td>
<td>0.0845</td>
</tr>
<tr>
<td>wR2 (all data)</td>
<td>0.1290</td>
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</table>

(CCDC 1010287)

Table ST2: The geometry of the Fe site surroundings in [Fe(Me₂-bpy)₃][NCSe]₂ · 3(H₂O)

<table>
<thead>
<tr>
<th>Fe-N bonds (Å)</th>
<th>100 K</th>
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<tbody>
<tr>
<td>Fe-N1</td>
<td>1.969(2)</td>
</tr>
<tr>
<td>Fe-N2</td>
<td>1.963(2)</td>
</tr>
<tr>
<td>Fe-N3</td>
<td>1.961(2)</td>
</tr>
<tr>
<td>Fe-N4</td>
<td>1.968(2)</td>
</tr>
<tr>
<td>Fe-N5</td>
<td>1.978(2)</td>
</tr>
<tr>
<td>Fe-N6</td>
<td>1.980(2)</td>
</tr>
</tbody>
</table>
**Figure S1:** Evolution of the crystal edges size and angle determined from optical microscopy images at 160 °C.
Figure S2: IR spectra of the powder of precursor recorded at 293 K before and after the thermal reaction. Inset: expansion showing the frequency range of ν_{NC}.

Figure S3: TEM images showing the 460 and 56 nm particles that, as described in the text, simultaneously precipitate by sudden addition of the ethanolic solution of precursor in toluene.
Figure S4: Superimposition of the temperature dependence of $\chi_{MT}$ reported for Fe(Me$_2$-bpy)$_2$(NCSe)$_2$.H$_2$O (in A. J. Cunningham et al, *J. Chem. Soc. Dalton Trans.*, 1972, 2155) and the one of the compound prepared by thermal treatment of [Fe(Me$_2$-bpy)$_3$](NCSe)$_2$.3H$_2$O.

Figure S5: Raman spectra recorded for [Fe(Me$_2$-bpy)$_3$](NCS)$_2$.3H$_2$O before (left) and after (right) the thermal treatment. The change of coordination sphere resulting from the solid heating is manifested by the set of vibrational peaks and their temperature dependence (in the table below), more specifically $\nu_{NC} = 2064$ and 2100sh, 2106 (200 K) or 2061, 2071, ~2100 (370 K) cm$^{-1}$ for the cationic and neutral complex respectively. Markers of both species are also identified in the low frequency range.
Table ST3: Raman data characterizing [Fe(Me₂-bpy)₃](NCSe)₂.₃H₂O (200 K) and Fe(Me₂-bpy)₂(NCSe)₂ (370 and 200 K).

<table>
<thead>
<tr>
<th>Compound</th>
<th>T (K)</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>Bulk</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td>Bulk after thermal treatment</td>
<td>200</td>
<td>2107, 2100,</td>
</tr>
<tr>
<td>Bulk after thermal treatment</td>
<td>370</td>
<td>~2100</td>
</tr>
<tr>
<td>Fe(Me₂-bpy)₂(NCSe)₂</td>
<td>370</td>
<td>2071, 2061, 1618, 1 551, 1483, 1416, 1379, 1317, 1275, 1268, 1201, 1029, 1023, 746, 673vw, 623, 556, 550, 532, 452, 403vw, 366vw, 354vw, 335vw, ca280vw, 261vw, 230.</td>
</tr>
</tbody>
</table>

In bold are indicated the frequencies that specifically appear for one compound (cationic, neutral) or one spin state (LS at 200 K and mixture of LS and HS forms at 370 K).

The $\nu_1$ NC(NCSe) frequencies are pointed at 2075/2065 (HS) and 2113/2106 (LS) cm⁻¹ for Fe(phen)₂(NCSe)₂.

The frequencies at 530.5, 527.0 cm⁻¹ in Fe(phen)₂(NCSe)₂ (in E. König et al Spectrochimica Acta, 1967, 23A, 45; P. Güttlich Struct. Bond. 44, Springer-Verlag, Berlin, 1981, pp83-195) ascribed to $\nu$Fe–N(NCSe) are found here at 532 cm⁻¹.
Figure S6: Raman spectra of nanoparticles of Fe(Me2-bpy)2(NCS)2 recorded at different temperatures (a) 1.2 µm microparticles, (b) in-PMMA 460 nm nanoparticles; (c) in-PMMA 56 nm nanoparticles
Figure S7: Comparison between the points (Δ bulk, ● 1.2 μm, ◦ 460 nm, ▲ 56 nm) corresponding to the variation of the relative intensity of the LS peak from Raman measurements and the HS fraction curves determined from magnetic measurements (dashed lines with the related colors). The observed discrepancies at low and high temperatures can be accounted for by uncertainties associated to the cases in which the HS fraction ~ 0 (or for highly diluted samples).