Spin-Crossover Nano- and Micrometric Rod-Shaped Particles Synthesized in Homogeneous Acid Media

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Acidic conditions have been used for the elaboration of spin-crossover (SCO) nano- and microparticles of BF₄ derivatives of a (triazole)iron complex. Modifying both the acid (HBF₄) concentration and the synthetic method (reaction and evaporation rate), rods of various sizes ranging from 100 nm to ca. 50 μm were obtained. The morphologies of the particles were probed by transmission electronic microscopy (TEM) and high-resolution transmission electronic microscopy coupled quantified energy-dispersive X-ray spectroscopy (HRTEM-EDX), elemental analysis, differential scanning calorimetry (DSC), NMR spectroscopy, and thermogravimetric analysis (TGA) were used to determine the fine compositions of the different samples. All these characterizations revealed a correlation between the size of the rod-shape particles and their composition, the smaller rods corresponding to the [Fe(Htrz)₂(trz)]BF₄ complex (form A; Htrz = 1,2,4-triazole and trz = 1,2,4-triazolato), and the larger ones to the [Fe(Htrz)₃]BF₄·3H₂O derivative (form B). The SCO properties were investigated by optical, magnetic, and Mössbauer measurements.

Introduction

Since the first reports of the spin transition (ST) phenomenon, several hundreds of spin-crossover complexes have been synthesized and characterized because of their potential applications, for example, as molecular memories, switching devices and sensors.[1,2] One of the still great challenges underlying the search for such molecule-based functional materials is the production of systems that exhibit switching properties at around room temperature and have a large hysteresis loop. (triazole)Fe⁺ complexes[3,4] with a 1D chain[5] are an important family of compounds that present such properties. In 1977, Hasnoot et al. reported the first example of such a compound, the [Fe(Htrz)₂(trz)][BF₄] complex[6] (Htrz = 1,2,4-triazole; trz = 1,2,4-triazolato), and its study was completed in 1994 by Kahn and co-workers.[7] They prepared several compounds depending on the experimental conditions. Using a water/ethanol mixture or methanol as solvent, two polymorphs of the [Fe(Htrz)₂(trz)][BF₄] derivative were obtained, whereas the use of a highly diluted methanol solution led to the precipitation of the [Fe(Htrz)₃]BF₄·3H₂O derivative, which exhibits a phase transformation (phase α to phase β) upon heating at ca. 440 K. Only the β phase showed an abrupt ST at around room temperature with a narrow hysteresis of ca. 6 K, but it is metastable and changed back to the α phase after several weeks with a rather abrupt transition at ca. 335 K. On the other hand, the more stable [Fe(Htrz)₂(trz)][BF₄] polymorph presents a large hysteresis loop of 50 K centered at 370 K. All these appealing properties can be exploited only if small and organized objects are fabricated. Indeed, if we look at the morphologies of the elements forming the bulk samples, rather polydisperse and micrometer-sized particles are observed. It is also interesting to note that in comparison with the rather spherical shaped particles encountered in the majority of the bulk samples of this family,[8] rod-like particles with lengths ranging from 300 to 800 nm were observed for the bulk sample of the [Fe(NH₂trz)₃][NO₃]₂ derivative.[9] In studies of the effects of size reduction on spin-crossover properties, different methods have been used to obtain controlled-size and monodisperse nanoparticles based on these materials. Following the pioneering work of Létard and co-workers, several groups used the reverse micelle technique or other matrices (heterogeneous media) to obtain such nanoparticles with sizes ranging from 6 to 1000 nm.[10–16] The particles were found to have rather nanoplaque-like morphologies. Our group has also used homogeneous media to obtain such types of nanoparticles.[17] Using different stabilizing agents, it was possible to obtain different sizes but also different shapes of micro- and nanoparticles. For example, by using triton X, a non-ionic polymeric amphiphilic compound, as stabilizers, nanorod-shaped particles with lengths ranging from 200 to 1000 nm were obtained, their widths ranging between 20 and 40 nm. As demonstrated in recently
published papers, such anisotropically shaped particles can be important for their organization at surfaces or between electrodes, notably for the measurement of their electrical and transport properties. In this paper, we report on an original method for the elaboration of nano- and micro-rods of both \([\text{Fe(Htrz)}_2(\text{trz})](\text{BF}_4)\) (form A) and \([\text{Fe(Htrz)}_3]_{-} (\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}\) (form B) derivatives of controlled size.

**Results and Discussion**

The rods were elaborated in a homogeneous medium without any stabilizing agent by just mixing \(\text{Fe(BF}_4)_2 \cdot 6\text{H}_2\text{O}\) and the Htrz ligand in the presence of different concentrations of HBF$_4$ in water. The first attempts led inexorably to the formation of unexpected samples containing Si atoms, which can be explained by the presence of SiF$_6$ anions formed when the walls of the glass (SiO$_2$) containers dissolve in HBF$_4$, replacing the BF$_4$ counter anions in the complex. The presence of such Si atoms was revealed by high-resolution scanning transmission electron microscopy coupled quantified energy dispersive X-ray spectroscopy (HRSTEM-EDX; see the Supporting Information). This undesirable complex does not present any spin-crossover properties and remains in the high-spin (HS) state irrespective of the temperature. To avoid this problem, all the syntheses were performed in plastic containers. Thus, on increasing the concentration of tetrafluoroboric acid from 0.1 to 5 wt.-% and modifying the rate of evaporation of the solvent and the synthetic method (see Table 1 and Figure S34 in the Supporting Information), crystalline purple powders were obtained after an increasing period of time ranging from a few minutes to ca. 1 month.

For a 5 wt.-% acid concentration, no precipitation was observed by using a low rate of evaporation comparable to that used for the elaboration of samples 1–5. Therefore, the rate of evaporation was increased, leading to samples 6 and 6’ (see the Exp. Sect. for details). Sample 7 was obtained with 2 wt.-% acid by liquid/liquid diffusion. In comparison with the previously reported bulk synthesis of this complex, the presence of acid lengthens the crystallization process, and we have good reason to believe that the acid solution slows the deprotonation of the Htrz ligand precluding the rapid precipitation of the \([\text{Fe(Htrz)}_2(\text{trz})](\text{BF}_4)\) complex.

The compositions of the samples were studied by Raman and IR spectroscopy, elemental analysis, NMR spectroscopy, thermogravimetric analysis (TGA), and X-ray powder diffraction, and the morphologies of the powders were probed by TEM and HRTEM-coupled EDX spectroscopy.

Selected IR spectra of selected samples are shown in Figure 1 (see the Supporting Information for more complete IR spectra for all samples). Samples 1–4 clearly exhibit spectra similar to that of the \([\text{Fe(Htrz)}_2(\text{trz})](\text{BF}_4)\) bulk sample, in particular, with vibrational modes at 1536 and 1497 cm$^{-1}$, which can be attributed to the stretching deformation of the protonated and unprotonated ligands, respectively. In contrast, the IR spectrum of sample 5, obtained in the presence of a higher acid concentration, presents different features in this part of the spectrum with the quasi-disappearance of the vibrational mode at 1497 cm$^{-1}$. More accurate quantitative analyses of the samples were realized by means of NMR analysis (see below). Moreover, the presence of a broad peak at ca. 3600 cm$^{-1}$, characteristic of the presence of water, tends to lead to the assignment of sample 5 as the \([\text{Fe(Htrz)}_3]_{-}(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}\) derivative.

![Figure 1. IR spectra of the bulk and samples 1, 5, and 6 at 293 K.](image)

Samples 6 and 6’ obtained in the presence of the highest concentration of acid (5 wt.-%) and at higher rates of evaporation give solutions composed of a mixture of \([\text{Fe(Htrz)}_2(\text{trz})](\text{BF}_4)\) and \([\text{Fe(Htrz)}_3]_{-}(\text{BF}_4)_2 \cdot 3\text{H}_2\text{O}\) as the vibrational mode at 1497 cm$^{-1}$ is clearly present but with a lower intensity compared with those in samples 1–4. This implies that both the acid concentration and the rate of evaporation influence the composition and also the size of the particles (see the TEM analysis below).

**Table 1. Sample preparation, size, and composition (ordered in increasing size).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>HBF$_4$ [wt.-%]</th>
<th>Synthetic method</th>
<th>Evaporation speed</th>
<th>Time</th>
<th>Size</th>
<th>Yield [%]</th>
<th>Composition (form)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>direct mixture</td>
<td>slow</td>
<td>15 min</td>
<td>100 ± 14 nm</td>
<td>72</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>direct mixture</td>
<td>slow</td>
<td>1 hour</td>
<td>640 ± 100 nm</td>
<td>62</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>direct mixture</td>
<td>slow</td>
<td>1 day</td>
<td>1.1 ± 0.1 µm</td>
<td>38</td>
<td>A</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>direct mixture</td>
<td>slow</td>
<td>3 days</td>
<td>1.4 ± 0.3 µm</td>
<td>33</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>direct mixture</td>
<td>very slow</td>
<td>5 days</td>
<td>4.5 ± 0.9 µm</td>
<td>24</td>
<td>mixture of A and B</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>direct mixture</td>
<td>slow</td>
<td>1 month</td>
<td>10 ± 2 µm</td>
<td>33</td>
<td>mixture of A and B</td>
</tr>
<tr>
<td>6’</td>
<td>5</td>
<td>direct mixture</td>
<td>fast</td>
<td>1 week</td>
<td>≥40 µm</td>
<td>24</td>
<td>mixture of A and B</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>liquid/liquid diffusion</td>
<td>fast</td>
<td>1 month</td>
<td>25 ± 10 µm</td>
<td>33</td>
<td>mixture of A and B</td>
</tr>
</tbody>
</table>

**Table 1.** Sample preparation, size, and composition (ordered in increasing size).
Raman spectra were acquired in both LS ($T = 400$, 350, and 370 K for 3, 5, and 6, respectively) and HS ($T = 250$ K for 3 and 6 and $T = 220$ K for 5) states (Figure 2 and the Supporting Information). These Raman spectra compare well with those reported previously.[21,22] In the region of the spectra considered, only the spectral feature at ca. 1300 cm$^{-1}$ can be used to distinguish the two compounds, namely the double-band character originating from the presence of the two different trz and Htrz ligands. The LS mode at 1311 cm$^{-1}$ (1308 cm$^{-1}$ in the HS state) is due to the Htrz ligand, and the band at 1285 cm$^{-1}$ (1282 cm$^{-1}$ in the HS state) is due to the trz ligand. The ratio of the areas of the trz and Htrz bands is approximately 1:2, in agreement with the stoichiometry of trz and Htrz in 3. In sample 5, only a residual trace of [Fe(Htrz)$_2$(trz)]($\text{BF}_4$) is observed (vibrational mode at 1285 cm$^{-1}$), whereas a mixture is clearly revealed for sample 6 (broadening of the vibrational mode at 1310 cm$^{-1}$).

Detailed compositions of the samples were also obtained by combined thermogravimetric (see Figure S5 in the Supporting Information) and CHN elemental analyses, which revealed the absence of water molecules for pure [Fe(Htrz)$_2$-
Figure 4. Solid-state $^1$H, $^{13}$C, and $^{19}$F NMR spectra of samples 3, 5, and 6 at 293 K.

$(\text{trz})[(\text{BF}_4)]$ samples 1–4 and 3', whereas ca. 3 molecules of water per iron atom were identified for pure $[\text{Fe(HTrz)}]_3-(\text{BF}_4)_2\cdot3\text{H}_2\text{O}$ samples 5 and 7. With regard to samples 6 and 6', approximately 1.5 molecules of water per iron atom were identified, in agreement with mixed samples incorporating about 40% of the $[\text{Fe(HTrz)}_2(\text{trz})](\text{BF}_4)$ derivative. In fact, higher concentrations of acid, which preclude the deprotonation of the HTrz ligand, and a low rate of evaporation of the complex solution lead to a slow stabilization of the fully protonated ligand $[\text{Fe(HTrz)}_3(\text{BF}_4)_2]\cdot3\text{H}_2\text{O}$ derivative.

TEM and HRTEM-EDX analyses were used to determine the shapes, sizes, and compositions of the particles. Figure 5 shows a representative TEM image for each sample (1–7, 3’, and 6’; see the Supporting Information for complementary images). Each sample displays similar particle morphology, but form rods of different lengths. We can observe that control of the experimental conditions and in particular the HBF$_4$ concentration permits us to obtain a series of nano- and microrods with sizes ranging from 100 nm to longer than 40 μm. It is interesting to note that all the experiments were repeated at least twice and that similar particle sizes were obtained.

The TEM image of sample 1 shows two orientations of the crystals, parallel and perpendicular to the grid surface; they exhibit a mean length of 100 nm and a mean section of about 10 nm. Increasing the acid concentration from 0.1 to 3 wt.-%, rods of $[\text{Fe(HTrz)}_2(\text{trz})](\text{BF}_4)$ with sizes of 100 nm to 1 μm were obtained. The average rod size of this derivative was increased to ca. 4 μm with 2 wt.-% HBF$_4$ and...
a reduction of the rate of evaporation of the solution (sample 3). Then, by increasing further the concentration of acid (4 wt.-%) and the period of the crystallization process, longer (ca. 10 μm) and pure rods of [Fe(Htrz)3](BF4)2·3H2O were obtained instead of the smaller [Fe(Htrz)2–(trz)](BF4) rods. Similar experiments using 5 wt.-% HBF4 and a higher rate of evaporation of the solvent led to the formation of mixtures of short [Fe(Htrz)2(trz)](BF4) rods and long [Fe(Htrz)3](BF4)2·3H2O rods. To go further, and with the objective of obtaining even longer and pure rods, a liquid/liquid diffusion synthetic method was used to reduce the speed of the reaction while maintaining a slow evaporation of the solution. Indeed, by using a 2 wt.-% HBF4 solution, pure [Fe(Htrz)3](BF4)2·3H2O rods with a mean size larger than 40 μm were obtained (sample 7). It is interesting to note that the crystallinity of these long rods is not sufficient for single-crystal X-ray measurements (even by using a synchrotron source). HRTEM-EDX was also employed to characterize the composition of a single rod (see the HRTEM study of sample 6 in Figure S15 in the Supporting Information) revealing the presence of iron atoms.

Calorimetric data (see Figure S17 in the Supporting Information) were recorded in heating and cooling modes at 5 K min⁻¹ to evaluate the enthalpy (ΔH) and entropy (ΔS) variations associated with the spin transitions of selected dehydrated samples (obtained by preliminary heating at 420 K). For the pure [Fe(Htrz)2(trz)](BF4) sample 3, the DSC curve shows a singularity at T_{1/2(\uparrow)} = 351 K and T_{1/2(\downarrow)} = 383 K for the cooling and heating modes, respectively, whereas for the pure [Fe(Htrz)3](BF4)2·3H2O sample 5, these singularities appear at T_{1/2(\downarrow)} = 289 K and T_{1/2(\uparrow)} = 293 K. In comparison with the magnetic measurements (see below), the slight deviation of the transition temperature can be associated with the difference in the heating and cooling rates. The estimated variations in ΔH and ΔS measured in the dehydrated forms are 20 and 16 kJ mol⁻¹ and 56 and 61 JK⁻¹ mol⁻¹ for samples 3 and 5, respectively. These values are typical for iron(II) spin-crossover compounds.

Complementary to a magnetic investigation and due to the drastic change in color accompanying the spin transition (ST), it is of obvious interest to study the optical behavior of the compounds in the visible range. Figure 6 allows comparison of the spin-transition behavior as measured by magnetic and optical reflectance for representative samples 2, 5, and 6 (see also the Supporting Information for the measurements on all samples). The different samples were cycled between 220 and 400 K after preliminary thermal treatment to achieve dehydroxylation. It is interesting to note that the dehydration of the [Fe(Htrz)3](BF4)2·3H2O sample leads to a decrease in the transition tempera-

![Figure 6. Thermal variation of the magnetic and optical measurements of samples 1, 5, and 6 (dehydrated samples).](image)
ture, the [Fe(Htrz)2(trz)](BF4) being unsolvated. As expected, samples 1-4 and 3' with the same composition as the bulk sample present similar properties with an abruptness of the transitions in both the heating and cooling modes. The critical temperatures are $T_{1/2}(1) = 352$ K and $T_{1/2}(1) = 397$ K for sample 1, whereas a narrow hysteresis is observed for the longer rods of samples 2-4 and 3' ($T_{1/2}(1) = 350$ K and $T_{1/2}(1) = 380$ K). This effect, which has already been observed for similar rod-shaped particles coated in SiO2, can be explained by the morphology of the particles and the associated structural organization of the chains. For samples 5 and 6, the spin loop is centered below ($T_{1/2}(1) = 265$ K and $T_{1/2}(1) = 278$ K) and at room temperature ($T_{1/2}(1) = 278$ K and $T_{1/2}(1) = 300$ K), respectively. Sample 6 (and also sample 6') exhibits intermediate transition temperatures in comparison with those measured for samples 1 and 5 and not the superposition of different singularities, which suggests that irrespective of the size of the rods in the mixed samples, the two forms A and B are randomly present. This result underlines that, although a certain threshold of acid concentration is necessary, the low rate of evaporation remains the driving force for obtaining pure form B of the complex.

We also recorded the $^{57}$Fe Mössbauer spectra of samples 3, 5, and 6 at 293 K (see Figure S33 in the Supporting Information). As expected for sample 3, the spectrum consists of one doublet with an isomer shift of 0.418(6) mm s$^{-1}$ and a quadrupole splitting of 0.286(9) mm s$^{-1}$ attributed to the LS state, with no residual HS state observed. In contrast, two doublets with an isomer shift of 0.41(1) [1.036(8)] mm s$^{-1}$ and a quadrupole splitting of 0.20(2) [2.70(2)] mm s$^{-1}$ attributed to the LS [HS] state are observed for sample 5, in agreement with the magnetic data for its hydrated form. Moreover, although sample 6 corresponds to a mixture of complexes, only one LS doublet is observed.

**Conclusions**

By using simple homogeneous acid media it has been possible to synthesize rod-shaped surfactant/polymer-free (triazole)Fe complex particles of various sizes with different chemical compositions. Physical characterization revealed a correlation between the size of the particles and their composition, the smaller rods corresponding to the [Fe(Htrz)$_2$(trz)](BF$_4$) complex with a spin transition localized at high temperature ($T_{1/2}(1) = 352$ K and $T_{1/2}(1) = 397$ K), with the longer rods corresponding to the fully protonated [Fe(Htrz)$_3$][BF$_4$]$_2$·3H$_2$O derivative with a spin transition just below room temperature ($T_{1/2}(1) = 265$ K and $T_{1/2}(1) = 278$ K). In fact, high concentrations of acid, which preclude the deprotonation of the Htrz ligand, associated with a slow rate of evaporation of the complex solution lead to a slow stabilization of long rod-shaped [Fe(Htrz)$_3$][BF$_4$]$_2$·3H$_2$O particles, whereas short rod-shaped [Fe(Htrz)$_2$(trz)][BF$_4$] particles are obtained with low acid concentrations. Thus, we have demonstrated that not only the size but also the morphology of the particles can be tuned for a considered material. These findings could be very useful for the specific organization of these bi-stable objects by using, for example, the soft lithographic capillary assembling technique or dielectrophoresis in the competition for understanding spatio-temporal behavior and also for transport measurements and the switching of individual objects that constitute one of the foremost paradigms in molecular electronics.

**Experimental Section**

**General:** All solvents and reagents were purchased from Sigma–Aldrich and used without further purification.

**Synthetic Procedure:** Samples 1-5 were prepared by rapidly mixing two aqueous solutions (with 0.1, 0.5, 2, 3, and 4 wt.% of HBF$_4$, respectively) containing Fe(BF$_4$)$_2$·6H$_2$O (225 mg, 0.33 mol L$^{-1}$) and the 1,2,4-triazole ligand (130 mg, 0.94 mol L$^{-1}$). The resulting 2 mL of limpid solution was left to let the solvent slowly evaporate at room temperature, the flask being half covered. After a specific period of time, the flocculates were centrifuged, washed with distilled water (10 mL) and absolute ethanol (30 mL), and finally dried under vacuum. Sample 3' was prepared as for sample 3 (2 wt.% HBF$_4$), but the speed of evaporation was decreased by opening less the cover of the flask (see Figure S34 in the Supporting Information). Samples 6 and 6' were prepared with 5 wt.% of HBF$_4$, but the speed of evaporation was increased (use of this acid concentration and the same slow evaporation as that used for the elaboration of samples 1-5, precipitation took several months). Sample 7 was prepared by using the same reactant concentrations as for sample 3 but a liquid/liquid (water/water) diffusion synthetic method was used instead of a direct mixture of the two reagents. A bulk sample obtained by using the same concentrations in aqueous solution in the absence of acid was synthesized as a reference sample.

Elemental analyses: calcd. for [Fe(Htrz)$_2$(trz)][BF$_4$]: C 20.66, H 2.33, N 35.71; found C 20.64, H 2.31, N 35.64.


**Solid-state $^1$H NMR (400 MHz):** $\delta = 157.1$ (1 H, NH), 132 (1 H, NH), 7.9 (6 H, CH) ppm (3); $\delta = 15.5$ (3 H, NH), 8.8 (6 H, CH), 4.5 (H$_2$O) ppm (5); $\delta = 15.5$ (3 H, NH), 8.3 (6 H, CH), 4.2 (H$_2$O) ppm (6); $\delta = 15.6$ (3 H, NH), 8.9 (6 H, CH), 4.5 (H$_2$O) ppm (7).

**Solid-state $^{13}$C NMR (400 MHz):** $\delta = 151.9$ (4 C, CH), 160.1 (2 C, CH) ppm (3); $\delta = 156.2$ (6 C, CH) ppm (5); $\delta = 152.4$ (4 C, CH), 155.7 (6 C, CH), 160.2 (2 C, CH) ppm (6); $\delta = 155.9$ (6 C, CH) ppm (7).

**Size and Physical Measurements:** Particle sizes were determined by TEM using a JEOL JEM-1011 instrument (100 kV). High-resolution imaging was performed with a JEOL JSM 2100F instrument (200 kV) equipped with an SDD Bruker EDX detector (resolution:}
127 eV) for elemental analysis. Samples for TEM analysis were prepared by placing a drop (10 µL) of the nanoparticles suspended in ethanol on a carbon-coated copper grid. FTIR spectra were recorded at room temperature with a Perkin-Elmer Spectrum 100 spectrometer in ATR mode (resolution ca. 1 cm⁻¹) between 650 and 4000 cm⁻¹. Variable-temperature Raman spectra were acquired using a LabramHR (Horiba) Raman microspectrometer (resolution ca. 3 cm⁻¹) in conjunction with a Linkam THMS600 cryostage. The 632.8 nm line of an HeNe laser (0.1 mW) was focused on the sample by using a × 50 objective (numerical aperture = 0.5), which was also used to collect the scattered photons. The latter were filtered by using an edge filter, but were not analyzed for their polarization state due to the random orientation of the particles in the sample volume. Solid-state ¹H, ¹³C, and ¹⁹F NMR spectra were recorded with a Bruker Avance 400WB spectrometer. Zero-field ⁵⁷Fe Mössbauer spectra were recorded by using a flow-type liquid-nitrogen cryostat and a conventional constant-acceleration-type Mössbauer spectrometer; γ-rays were provided by a ⁵⁷Co(Rh) source (ca. 20 mCi). The samples (ca. 30 mg) were enclosed in a Plexiglass sample holder with an optimized diameter. The spectra were evaluated by assuming Lorentzian line shapes using the Recoil software.²³ The PXRD patterns of the samples were recorded at room temperature by using a Panalytical MPD XPertPro powder diffractometer [Cu-Kα₁, Ge(111) monochromator, X'Celerator detector] in the 2θ range 5–80° using a scan speed of 30° h⁻¹.

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