SUPPLEMENTARY INFORMATION

Photo-thermal plasmonic effect in spin crossover@silica/gold nanocomposite.

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1-Synthesis and characterization of samples 1-3

2-TEM, STEM and EDX analysis of samples 1-3

3-⁵⁷Fe Mössbauer, optical reflectivity and magnetic measurements of samples 1-3

4-Raman spectra of samples 1-3.
1-Synthesis and characterization of samples 1-3

Synthesis of SCO@SiO$_2$ (1).

Nanoparticles were prepared according to the method described in ref. 18 with some modifications. Two microemulsions were prepared. First, an aqueous solution of Fe(BF$_4$)$_2$·6H$_2$O (422 mg, 1.25 mmol in 1 mL H$_2$O) was added dropwise to a mixture of 0.1 mL of tetraethylorthosilicate (TEOS), 3.6 mL of Triton X-100, 3.6 mL of hexanol and 15 mL of cyclohexane. Then, a solution of H-trz (262 mg, 3.75 mmol in 1 mL H$_2$O) was added dropwise to another TEOS – Triton – hexanol – cyclohexane mixture with the same composition. The two microemulsions were quickly combined and 15 minutes later 0.2 mL of (3-mercaptopropyl)trimethoxysilane were added. The mixture was stirred for 24 h, followed by addition of ethanol to destroy the structure of the microemulsion. The nanoparticles were recovered by centrifugation, washed three times with ethanol and dried at 70 °C for 12 h.

To functionalize the surface of the nanoparticles with thiol groups, 50 mg of as prepared nanoparticles were suspended in 20 mL of absolute ethanol using an ultrasonic bath for 15 minutes. To the suspension obtained in such a way, 25 mL of (3-mercaptopropyl)trimethoxysilane were added. The mixture was stirred overnight at room temperature followed by refluxing for 2 h. To recover the modified nanoparticles, the mixture was cooled down, centrifuged and washed three times with ethanol.

Synthesis of SCO@silica/small gold Nps (2).

An aqueous solution of small gold nanoclusters (2-3 nm in diameter) was prepared by reduction of chloroauric acid with tetrakishydroxymethylphosphonium chloride (THPC) as described by Duff et al. in ref. 20. A freshly prepared gold nanocluster solution (2 mL) was added dropwise to the suspension of thiol-functionalized nanoparticles of 1 in ethanol (30 mL) upon vigorous stirring. This mixture was stirred for 20 minutes, then centrifuged and washed twice with ethanol. The nanoparticles were dried at 70 °C for 12 h.

Synthesis of SCO@silica/larger gold Nps (3). Sample 2 (20 mg) was re-dispersed in 30 ml of isopropanol using an ultrasonic bath and 5 mg of HAuCl$_4$ were added. To this suspension a solution of triethylamine in isopropanol was added until the colour change indicating the aurum reduction. Nanoparticles then were centrifuged, washed twice with ethanol and dried at 70 °C for 12 h.
Table S1. Elemental analysis of samples 1-3. (The proposed formulas for the compounds were concluded by elemental analysis (C, H, N, S) and EDX (Si, Fe, Au) measurements. Molecular weights were calculated and used to determine molar magnetic susceptibilities.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C / %</th>
<th>H / %</th>
<th>N / %</th>
<th>S / %</th>
<th>Calculated Formula</th>
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<td>1.51</td>
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Fig. S1. FTIR spectrum of the sample 1, silica and Triton X-100.
2-TEM, STEM and EDX analysis of samples 1-3

Figure S2: TEM images and size distribution diagrams of sample 1

Length = 154 ± 11 nm

Width = 88 ± 18 nm
TEM image of the corresponding particles synthesized in absence of (3-mercaptopropyl)trimethoxysilane during the micellar exchange.

**Figure S3**: TEM image of the gold nanoparticles and their size distribution diagram. Mean size is 2.1 nm.
**Figure S4:** HR STEM (a) EDX maps of Si (b), Si+Fe (c) and combined STEM EDX compositional map (d) of sample 1. The parasite signals on the area without any particle come from a Si pollution of the window of the detector.
Figure S5: TEM images and size distribution diagrams of sample 2

Length = 172 ± 11 nm

Width = 94 ± 15 nm

Gold seeds mean size 2.1 nm
Figure S6: TEM images and size distribution diagrams of sample 3

Length = 175 ± 16 nm

Width = 94 ± 11 nm

Gold nanoparticles mean size 14 nm
**Figure S7:** HRTEM image and EDX spectra of sample 2. EDX measurements were performed on the twined particles at three different positions. These localized compositional measurements are realized in ca. 10 nm² area. The characteristic EDX peaks spectra of Au, Fe, Si and Cu atoms are showed (Cu arises from the copper grid sample holder).

**Figure S8:** Darkfield STEM image of 2 (a) and STEM EDX compositional maps. All the data for mapping of Au (b), Si (c) and Si -Fe-Au (d) were collected from the square area indicated in the
STEM image. The parasite signals on the area without any particle come from a Si pollution of the window of the detector.
**Figure S9**: HRTEM image (a) and selected EDX measurement (b) on particles of sample 3. This compositional measurement is realized on the full image surface. The characteristic peaks belonging to Au, Fe, Si and Cu atoms are shown (Cu arises from the copper grid sample holder).
Figure S10: Dark field STEM image of 3 (a) and STEM EDX compositional maps. All the data for mapping of Au (b), Si (c) and Si-Fe-Au (d) were collected from the nanoparticle shown in the STEM image. The parasite signals on the area without any particle come from a Si pollution of the window of the detector.
Figure S11: Magnetic measurements on samples 1-3 through two successive thermal cycles. (The first/second cycle is plotted using full/empty triangles.)

<table>
<thead>
<tr>
<th>Sample</th>
<th>First thermal cycle</th>
<th>Second thermal cycle</th>
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<tr>
<td></td>
<td>( T^\uparrow[K] )</td>
<td>( T^\downarrow[K] )</td>
</tr>
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Figure S12: $^{57}$Fe Mössbauer spectrum of sample 2 at 80 K. The spectrum can be fitted with a doublet with an isomer shift $\delta = 0.482(5)$ mm/s vs. $\alpha$-Fe and a quadrupole splitting $\Delta Eq = 0.27(1)$ mm/s corresponding to an iron(II) LS.
Figure S13: Optical reflectivity ($\lambda=550$ nm) measurements on samples 1-2 through two consecutive heating-cooling cycles. Sample 3 did not display any color change during the thermal cycle because of its deep color.
4- Absorbance and Raman spectra of samples 1-3.

**Figure S14:** Raman spectra for 1 collected at consecutive laser power increase (from 22 to 2000µW, 632.8 nm laser excitation). The temperature was maintained constant at 100ºC during the experiment.

**Figure S15:** Raman spectra sequence for 2 collected at consecutive laser power increase (from 22 to 500µW respectively, 632.8 nm laser excitation). The temperature was constant at 100ºC during the experiment.
**Figure S16:** Raman spectra (\(\lambda=632.8\) nm) of 1 (left) and 2 (right) before (red) and after (black) the increase of the laser pump power (up to 2000\(\mu\)W for 1 and 500 \(\mu\)W for 2) (laser probe power is equal to 22 \(\mu\)W in each case).

**Figure S17:** Raman spectra (\(\lambda=632.8\) nm) of 3 recorded at room temperature for a laser power of 10\(\mu\)W.
**Figure S18:** Absorbance spectra of gold nanoparticles of 2 nm (black), nanocomposite 2 (green) and 3 (red). Measurements were performed on nanoparticle suspension in ethanol.