Electronic Supplementary Material (ESI) for ChemComm.

Graft of gold on spin-crossover nanoparticles: SCO@Au

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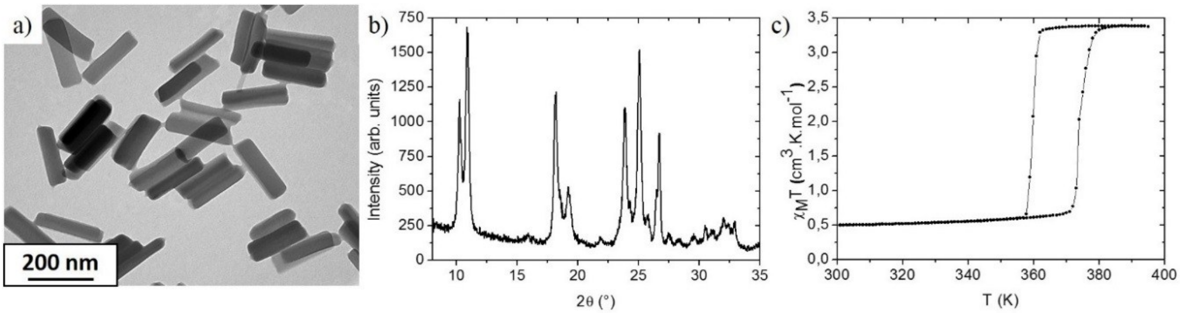
Supplementary material

ESI-1 characterization of the initial particles of [Fe(Htrz)$_2$(trz)](BF$_4$)

a) TEM images of the [Fe(Htrz)$_2$(trz)](BF$_4$) particles subsequently used for the grafting

b) PXRD of the [Fe(Htrz)$_2$(trz)](BF$_4$) particles subsequently used for the grafting

c) Squid measurements of the [Fe(Htrz)$_2$(trz)](BF$_4$) particles subsequently used for the grafting



These results perfectly match the usual [Fe(Htrz)$_2$(trz)](BF$_4$) properties (references below).

Examples of references for magnetic properties of nanoparticles of [Fe(Htrz)2(trz)](BF4):(a) D. Qiu, L. Gu, X. -L. Sun, D. -H. Ren, Z.-G. Gu, Z. Lia, *R. Soc. Chem. Adv.*, 2014, 4, 61313; (b) C. M. Quintero, G. Felix, I. Suleimanov, J. Sanchez Costa, G. Molnar, L. Salmon, W. Nicolazzi, A. Bousseksou, *Beilstein J Nanotechnol.*, 2014, 5; (c) M. Gimenez-Marqués, M. Luisa Garcia-Sanz de Larrea, E. Coronado, *J. Mater. Chem. C* 2015, 3, 7946-7953 ; (d) C. Bartual-Murgui, E. Natividad, O. Roubeau, *J. Mater. Chem. C* 2015, 3, 7916-7924

References for TEM and PXRD: L. Moulet, N. Daro, C. Etrillard, J.-F Létard, A. Grosjean, P. Guionneau, Magnetochemistry 2016, 2**(1)**, 10

PXRD : A. Grosjean, N. Daro, S. Pechev; L. Moulet, C. Etrillard, G. Chastanet, P. Guionneau, *Eur. J. Inorg. Chem.*, 2016, 1961-1966

ESI-2 Synthesis and characterization of the AuNP-PVP dispersions

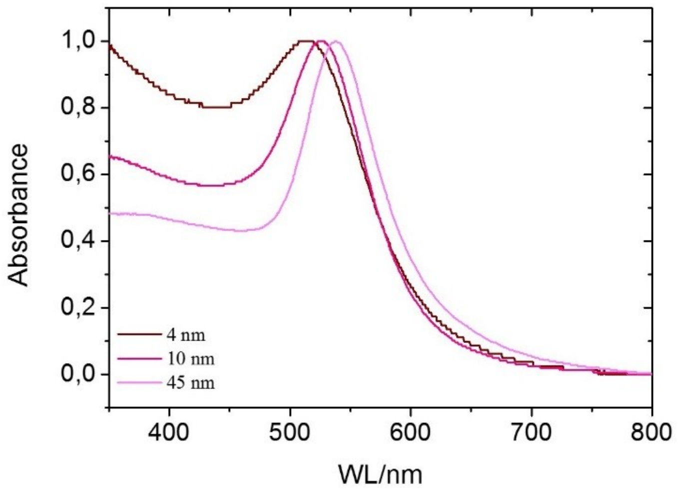
a) AuNP synthesis. The synthesis of the 45 nm size gold nanoparticles (AuNPs) followed the procedure reported by Puntes et al. [1]. Briefly, the synthesis consists on a slow and separate addition of gold salts ($KAuCl_4$, stock solution at 0.2% w/v) and a mixture of reducing/stabilizing agents (ascorbic acid and sodium citrate, stock solutions at 1% w/v respectively) during 45 min at room temperature to 20 ml of AuNPs seed solution. The solution was left to reflux for 1 h.

Gold nanoparticles (AuNp) of 10 nm diameter used in these experiments were prepared by citrate reduction method optimised from the classical protocol of Turkevich et al. [2], in order to obtain here 10 nm diameter nanoparticles with a highly monodisperse size distribution [3]. The procedure can be briefly described as follows: A volume of 400 mL of Milli-Q water is carried to boiling. Then a volume of 100 mL of an aqueous solution of 5.53 mM potassium tetrachloroaurate is added. The reaction medium is carried to the water reflux (110°C). The reduction of auric salts occurs upon addition of 50 mL of 3.4 mM sodium citrate dihydrate solution. The reaction is left 30 minutes to the water reflux and then cooled at room temperature. The average diameter measured by transmission electron microscopy is typically equal to 10.0 ± 0.5 nm and the concentration equal to 33 nM ($1.96\ 10^{16}$ particles/L).

For the 4 nm AuNP, a volume of 100 mL of solution at 0.25 mM of $HAuCL_4$ and 0.25 mM of tri-sodium citrate is firstly prepared. Then 3 mL of ice cold 0.1 M $NaBH_4$ solution is added to the solution all at once while stirring. The excess of $NaBH_4$ is after degraded by neutralization of the solution by adding 0.1 M HCl under control of pH.

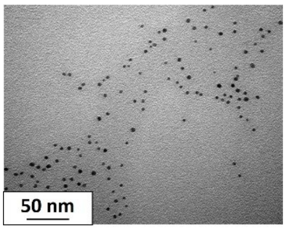
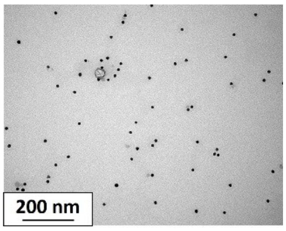
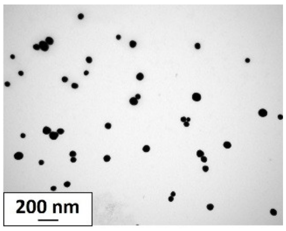
b) PVP wrapping. The as-synthesized AuNPs were incubated overnight in an aqueous solution of PVP (Mw=55000, 10 g L^{-1}). In order to remove the excess of PVP, the washings against ethanol were performed by centrifugation (2000g) for the 45 nm AuNPs dispersions and by tangential ultrafiltration (Amicon®, Millipore) using PSS membranes of 300 kDa cut-off for the 10 nm and 4 nm AuNPs dispersions. The volumes of washings are measured in order to reach a dilution coefficient of 10. Particles are then concentrated using 1g/L PVP in ethanol at approaching $2.2\ 10^{16}$ p/L for 45nm AuNPs, $1.63\ 10^{18}$ p/L for 10nm AuNPs and $3.7\ 10^{18}$ p/L for 4nm AuNPs.

c) Visible-UV spectra of the Au particles

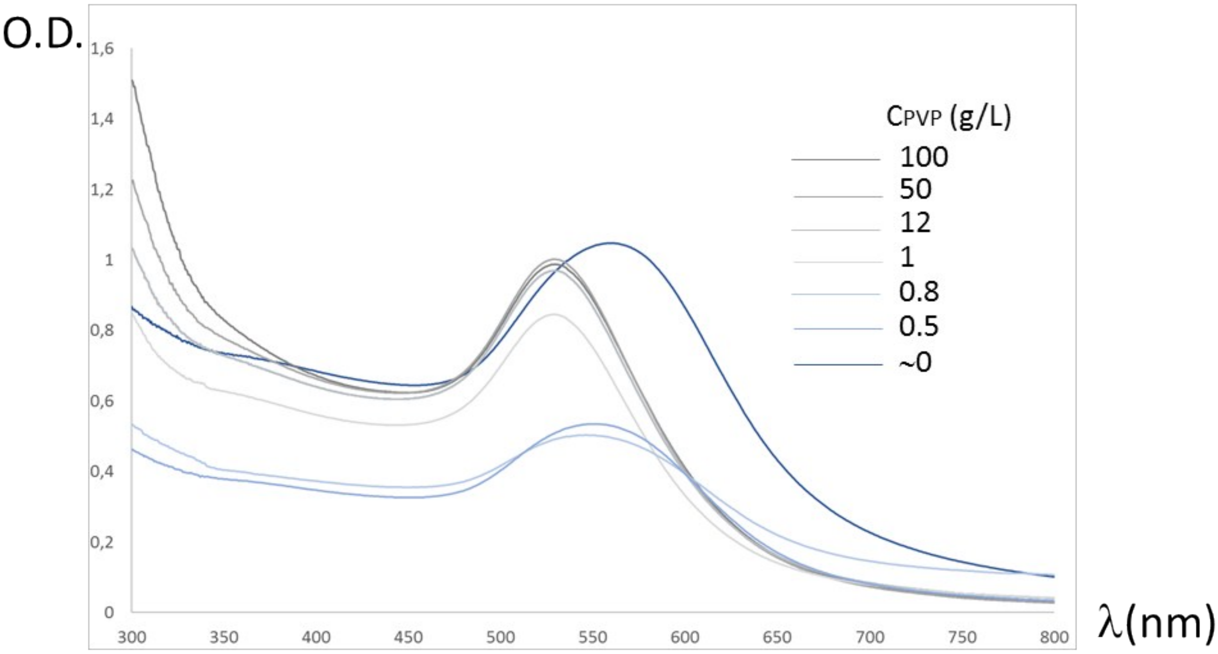


Normalized UV-vis absorption spectra of 4, 10 and 45 nm size AuNP-PVP dispersed in ethanol. The red shift observed between each sample is assigned to the increase of the particle size.

d) TEM images for Au particles of 4, 10 and 45 nm size

		
$C_{Au} = 3.7.10^{18}$ part/L	$C_{Au} = 1.63.10^{18}$ part/L	$C_{Au} = 2.6.10^{16}$ part/L

e) Colloidal stability of AuNPs in ethanol vs concentration of PVP (55kDa).



UV-Vis spectra showing the dependence of PVP concentration on the colloidal stabilization of gold NPs in ethanol. The large red shift of the SPR band maximum spectra associated with the broadening of the FWHM of the SPR band indicate the colloidal destabilization. The colloidal destabilization occurs for PVP concentration below 1 g/L after 24 h incubation.

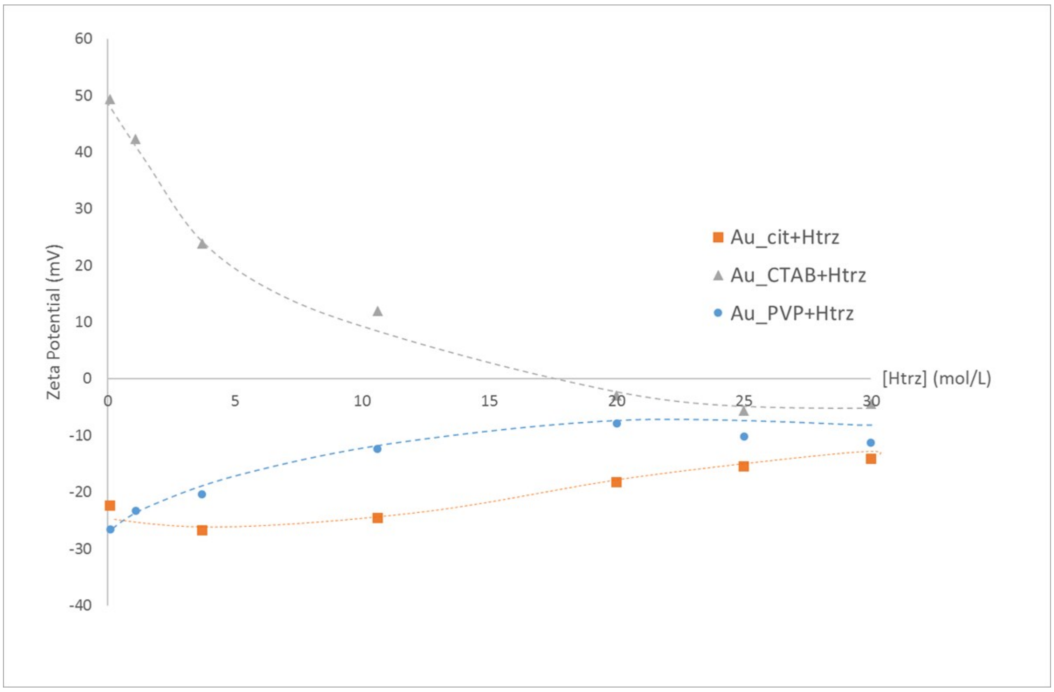
References:

1- N. G. Bastus, J. Comenge, V. Puntes, *Langmuir*, 2011, 27, 11098.

2- S. Renault, M. Baudrimont, N. Mesmer-Dudons, P. Gonzalez, S. Mornet, A. Brisson, *Gold Bulle*tin, 2008, 41(2), 116.

3- N. R. Jana, L. Gearheart, C. J. Murphy, *J. Phys. Chem. B.*, 2001, 105, 4065.

ESI-3 Ligand exchange by Htrz at AuNP surface monitored by zeta potential measurements



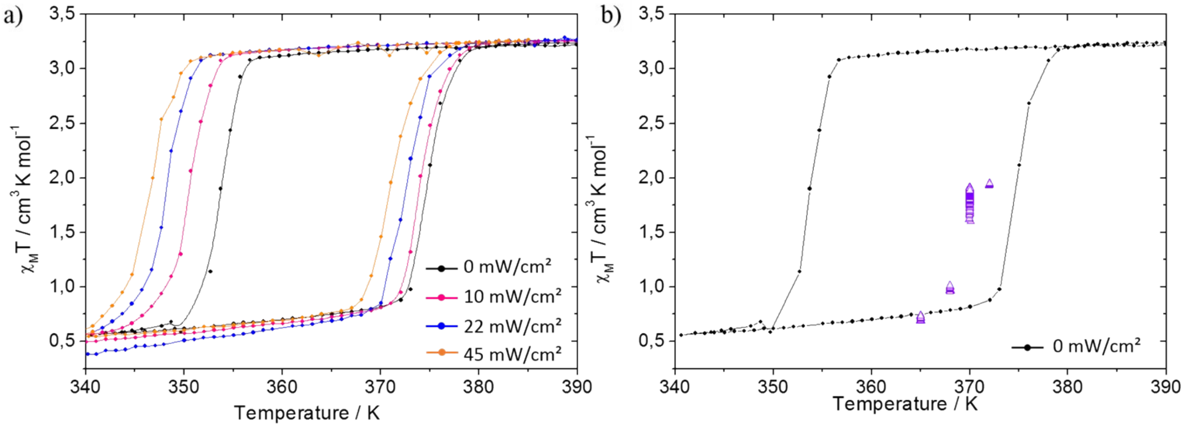
Zeta potential measurements of gold NPs stabilized with several type of ligands *vs* Htrz concentration performed in water.

Zeta potential measurements were performed on gold nanoparticles stabilized with different types of ligands (weak ones such as citrate and PVP, and a stronger amphiphilic ligand, CTAB (cetyltrimethylammonium bromide) which stabilizes the dispersion by forming a bilayer surrounding the NPs). Whatever the ligand type, it can be obviously observed the exchange manifested by the tendency of three potential profiles to tend towards the same potential value around -10 mV for saturating concentrations.

ESI-4 magnetic measurements on $[Fe(Htrz)_2(trz)](BF_4)$@AuNPs

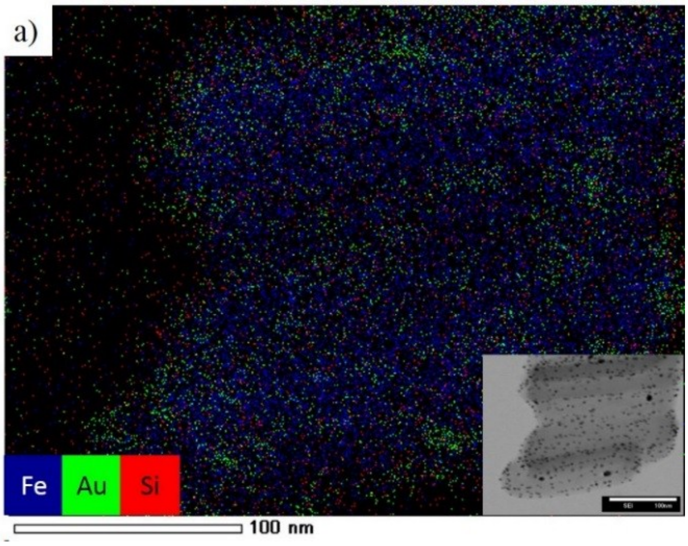
(a) Magnetic behaviour of $[Fe(Htrz)_2(trz)](BF_4)$@Au particles using 10 nm gold particles. The photocommutation is tested using different light intensities. No significant difference with the known $[Fe(Htrz)_2(trz)](BF_4)$ behaviour is seen here.

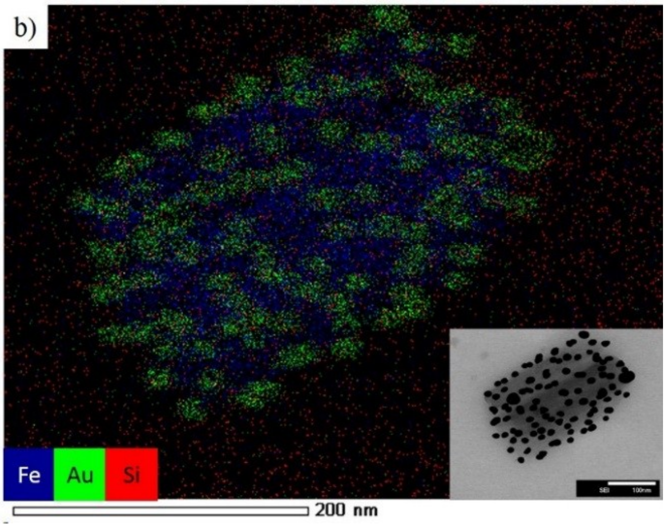
(b) Magnetic behaviour of $[Fe(Htrz)_2(trz)](BF_4)$@Au particles using 10 nm gold particles including a continuous irradiation effect at 45 mW/cm^2 (violet triangles).

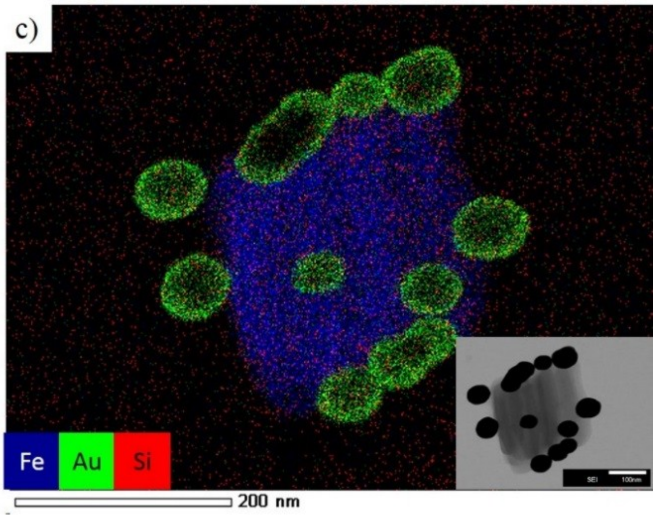


ESI-5 STEM EDX on [Fe(Htrz)$_2$(trz)](BF$_4$)@AuNPs

STEM-EDX of [Fe(Htrz)$_2$(trz)](BF$_4$)@Au particles with gold nanoparticles sizes of (a) 4 nm, (b) 10 nm and (c) 45 nm. Color code: blue for Fe, red for SiO$_2$, green for Au.







ESI-6 calculation of *n*

Article sketch: *"To monitor the effects of the initial gold-concentration on the final result, we define here the ratio Au:SCO. The notation 1:1 describes the situation where the n gold nanoparticles necessary to theoretically cover entirely one SCO [Fe(Htrz)$_2$(trz)](BF$_4$) particle are used. For instance the ratio 5:1 means that 5n gold nanoparticles are used while 1:4 means only one quarter of the n gold nanoparticles are used (details of calculation are provided in ESI). The first synthesis reported above corresponds therefore to the ratio 1:2. Note also that n is obtained from the relative values of the surfaces calculated from the dimensions of the SCO and gold particles. For instance, for 10 nm gold particles, n corresponds to 500 particles"*

The detail of the calculation performed to estimate *n* is given below:
The number *n* can be obtained by the ratio between the surface of one [Fe(Htrz)$_2$(trz)](BF$_4$) particle, denoted S_{TS}, and the optimized surface of contact of one Au particle, denoted S_{Au}.
The value for S_{TS} is determined from the TEM image. Since the particle are cylindrical (see TEM images in the present article and in ESI-1) the surface is obtained using the radius R and the length L. It is clear that homogenous sizes of particles must be obtained in the whole sample to get a reliable estimation. For the studied material, the rational control of these sizes is demonstrated in L. Moulet, N. Daro, C. Etrillard, J.-F Létard, A. Grosjean, P. Guionneau, Magnetochemistry 2016, 2(1), 10

To determine S_{Au}, since *n* must reflects the ideal situation, it is supposed that the spherical Au particles adopt a close packing around the SCO particles with r as the radius of the Au particle. In such conditions: $S_{Au}(\mathrm{nm}) = 2\sqrt{3} \times r^2$

Then:

$$n = \frac{S_{TS}}{S_{Au}} = \frac{(2\pi \times R \times L) + (2\pi \times R^2)}{2\sqrt{3} \times r^2}$$

Calculation for 10 nm Au particles and the [Fe(Htrz)2(trz)](BF4) particles used in this work:

$$n = \frac{S_{TS}}{S_{Au}} = \frac{(2\pi \times R \times L) + (2\pi \times R^2)}{2\sqrt{3} \times r^2} = \frac{(2\pi \times 30 \times 200) + (2\pi \times 30^2)}{2\sqrt{3} \times 5^2} = 500$$

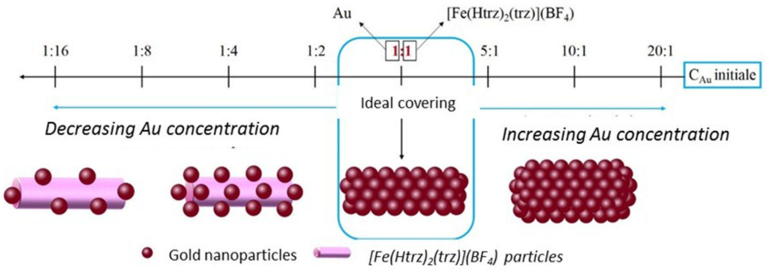
Concentrations and ratios used for each nanoparticle size: Considering a SCO particle size of 60 X 200 nm and a density of 1.977 calculated from XRD data (A. Grosjean, PhD Thesis of Bordeaux University, 2013), $m_{SCO} = 1.12\ 10^{-15}$ g/part

AuNP-45nm: *n* = 25, C20:1(AuNP-45nm) = 2.2 10^{16} p/L; C1:1(AuNP-45nm) = 1.1 10^{15} part/L; C1:1(SCO)=0.05 g/L.

AuNP-10nm: *n* = 500, C20:1 (AuNP-10nm) = 1.63 10^{18} p/L; C1:1(AuNP-10nm) = 8.15 10^{16} part/L; C1:1(SCO)=0.18 g/L.

AuNP-4nm: *n* = 782, C20:1 (AuNP-4nm) = 3.7 10^{18} p/L; C1:1(AuNP-4nm) = 1.85 10^{17} part/L; C1:1(SCO)=0.26 g/L.

Scheme that defines the Au:SCO ratio: 1:1 corresponds to the situation where *n* gold particles are used, other ratio are derived from that calculation (see the article sketch above):



ESI-7 Suggested formation mechanism of $[Fe(Htrz)_2(trz)](BF_4)$@AuNPs hybrid particles