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Post-synthetic modification mechanism for 1D spin crossover coordination polymers

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Materials and equipments

Commercial reactants and solvents were used directly without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained at 298 K in $CDCl_3$ or D_2O as internal reference and were recorded on a Bruker Avance 300 or a Bruker Avance 400, chemical shifts are reported in parts per million (ppm). Infrared spectra were recorded on a Perkin Elmer 1725 Spectrometer. Variable-temperature magnetic susceptibility data were obtained at cooling and heating rates of 4 K min−1 under a field of 1 kOe using a Quantum Design MPMS magnetometer. Powder X-ray diffraction patterns were recorded using a PANalytical X'Pert equipped with a Cu X-ray tube, a Ge(111) incident beam monochromator (λ = 1.5406 Å) and an X'Celerator detector. ^{57}Fe Mössbauer spectra have been recorded using a conventional constant-acceleration-type spectrometer

equipped with a 50 mCi ^{57}Co source and a liquid nitrogen cryostat; least-squares fittings of the Mössbauer spectra have been carried out with the assumption of Lorentzian line shapes using the Recoil software. Transmission electronic microscopy (TEM) was carried out using a 100 kV JEOL JEM-1011 (JEOL, Croissy Sur Seine, France). TEM samples were prepared by depositing on a carbon coated copper grid (400 mesh) a few drops of the nanoparticles suspended in ethanol.

S1.- Synthesis of bulk $[Fe(NH_2trz)_3](NO_3)_2$ (**1**)

2.62 g (10 mmol) of $Ba(NO_3)_2$ and 100 mg of ascorbic acid were dissolved in 20 mL of distilled water. In a separate flask 2.78 g (10 mmol) of $FeSO_4 \cdot 7H_2O$ were dissolved in 10 mL of distilled water. Both solutions were heated slowly until complete dissolution of the reagents. Then the solution containing the iron was added to the solution of barium nitrate, which resulted in an immediate precipitation of barium sulfate. The suspension, was left to cool down to room temperature and then centrifuged resulting in 30 mL of a 0.333 M solution of $Fe(NO_3)_2$.

2.52 g (30 mmol) of 4-amino-1,2,4-triazole were dissolved in 10 mL of ethanol, then 30 mL of a freshly prepared 0.333 M solution of $Fe(NO_3)_2$ was added to it under vigorous stirring; the mixture was left stirring during 3 h resulting in a pink slurry. It was centrifuged and washed 3 times with 20 mL of ethanol and then 3 times with 20 mL of diethyl ether, after which it was dried in the oven at 60°C, resulting in 2.76 g (65%) of the product.

S2.- Synthesis of nanoparticles of $[Fe(NH_2trz)_3](NO_3)_2$ (**1**)

Two equivalent micellar solution were prepared as follow; 160 mL of cyclohexane, 72 mL of *n*-pentanol and 57 g of triton X-100 were vigorously mixed. To this mixture 756 mg (9 mmol) of 4-amino-1,2,4-triazole dissolved in 20 mL of distilled water were added dropwise to obtain the first microemulsion, 20 mL of a 0.15 M $Fe(NO_3)_2$ solution were added dropwise to obtain the second microemulsion. These microemulsions were stirred at room temperature for about 15-20 minutes, until a clear solution was observed, then the second microemulsion was added to the first one and it was kept under vigorous stirring overnight. Then 500 mL of ethanol was added to destroy the microemulsion, the obtained nanoparticles were centrifuged and washed several times with ethanol to remove traces of the surfactant and then several times with diethyl ether. It was left to dry at room temperature resulting in 810 mg (64%) of the product.

S3.- General methodology for the Post-synthetic modification

50 mg of the SCO complex **1**, 300 μL of *p*-anisaldehyde and 2 mL of the solvent were suspended in an Ace pressure tube, then it was immersed in an oil bath at 90 °C and stirred for a certain period of time. Then the tube was immersed immediately in an ice-water-ethanol bath to stop the reaction and after 1 min, 5 mL of diethyl ether was added to the mixture. The mixture was centrifuged and washed 5 times with 10 mL diethyl ether and then dried in an oven at 60°C.

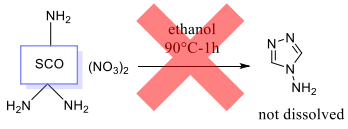
The quantification of the % of PSM was done by digestion of the samples using our previously reported methodology.[1] A standard solution of 1,3,5-trimethylbenzene in $CDCl_3$ and pentaerythritol in D_2O were prepared for each day of analysis (in order to avoid the evaporation of the solvent in the stock solution), this was done by weighting a known quantity of the standard (approximately 10 mg) in 5 mL of the solvent

in a volumetric flask. 2 mL of a 1M solution of K_2CO_3 in D_2O and 2 mL of $CDCl_3$ were added to a falcon tube with a known quantity of the SCO complex (each complex was thoroughly weighted, approximately 10 mg) and it was closed and stirred vigorously and sonicated for 15 min (or until completely dissolution of the SCO compound and the appearance of a yellow aqueous phase), the resulting mixture was then centrifuged allowing the separation of the organic and aqueous phase and an interlayer of iron residues. Under these conditions, the complex is destroyed and allows the non-coordinated ligands to be recovered (aminotriazole in the water phase and imine in the organic phase) and quantified; 0.4 mL of the $CDCl_3$ or D_2O digestion solution was taken and added to 0.2 mL of the corresponding standard solution, after which the ^{1}H-NMR was recorded. This procedure was repeated at least 2 times, and the reported results are the average.

S4.- Results of the PSM with different solvents

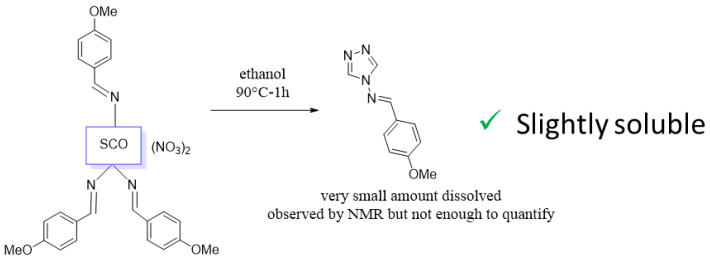
Time of reaction (min)	Methanol	Ethanol	Ethanol 96%	Butanol	Ethanol Toluene	Toluene	Dioxane	Octanol
10	18.8	8.7	14.8	---	---	---	---	---
20	87.5	17.5	48.3					
30	90.3	35.1	84.8					
40	95.4	86.6	97.9	0	0	0	0	0
50	100	94.0	---	---	---	---	---	---
60	100	98.0		7.2	0	0	0	0
70	---	100		---	---	---	---	---
90		---		54.3	0	0	0	0
120				100	60.0	0	0	0
180				100	100	0	0	6.5
240				---	100	0	0	24.1
1020					---	---	---	100
3960								100

Scheme S1.- Solubility experiments for the complex **1** and **2**

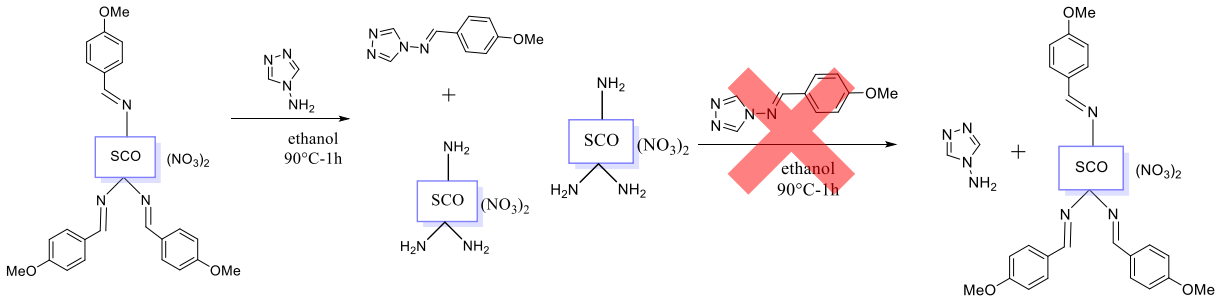


✓ If soluble
- C < 10^{-5}M

(by UV-Vis absorption)



Scheme S2.- Reaction of complex **2** and **1** with aminotriazole or imine correspondingly



✓ Exchange possible
✓ Transimination possible

✓ Exchange not possible
✓ Transimination no possible

Scheme S3.- Transformation of the functions of complex **1** in the presence of imine ligand

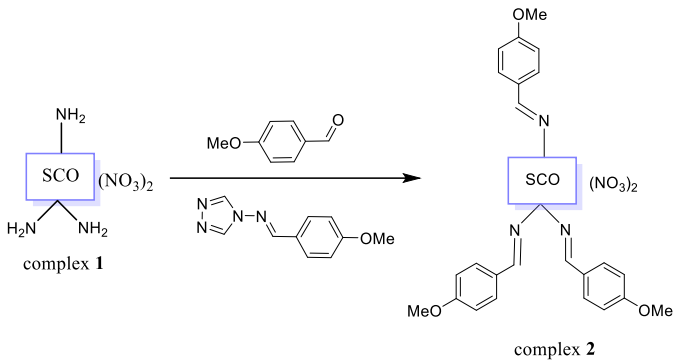


Figure S1.- Conversion of the aminotriazole ligand into the imine derivative in different solvents

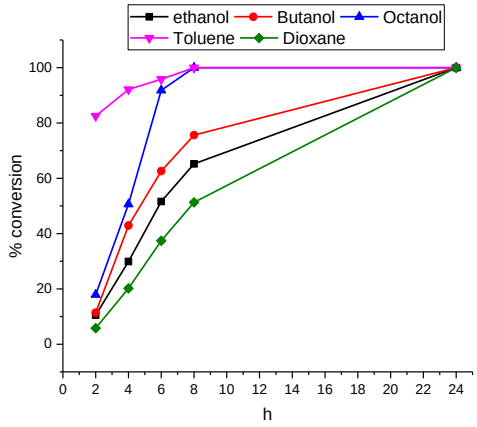


Figure S2.- Variable temperature magnetic measurements of the 100% PSM products obtained in different solvents

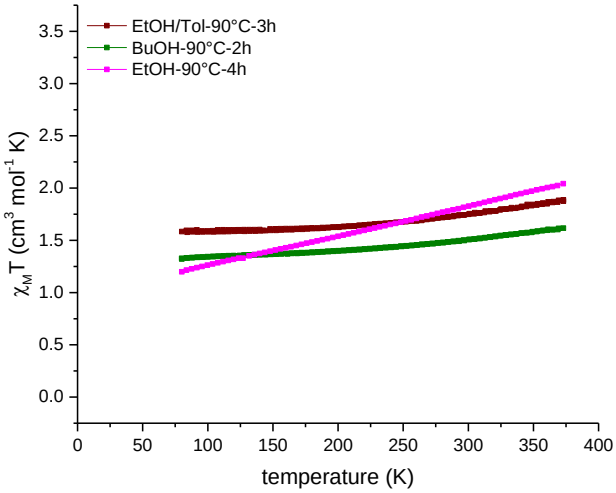
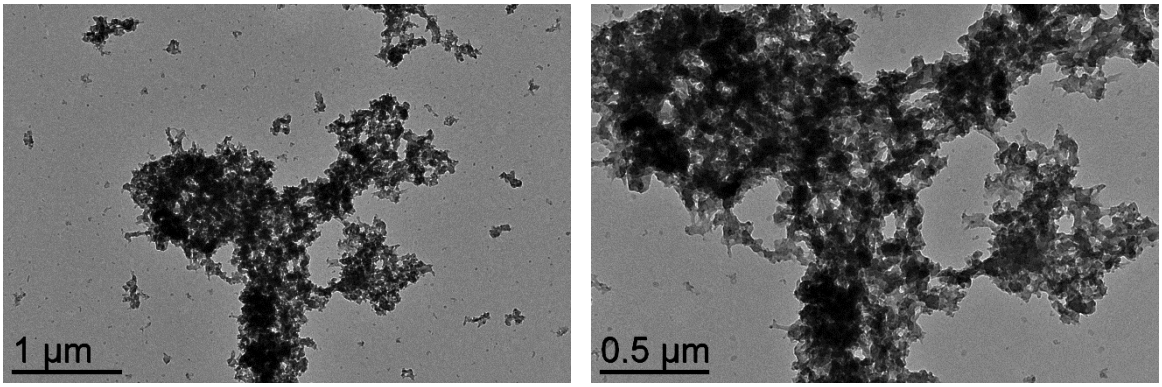


Figure S3.- TEM images of nanoparticles of complex **1**



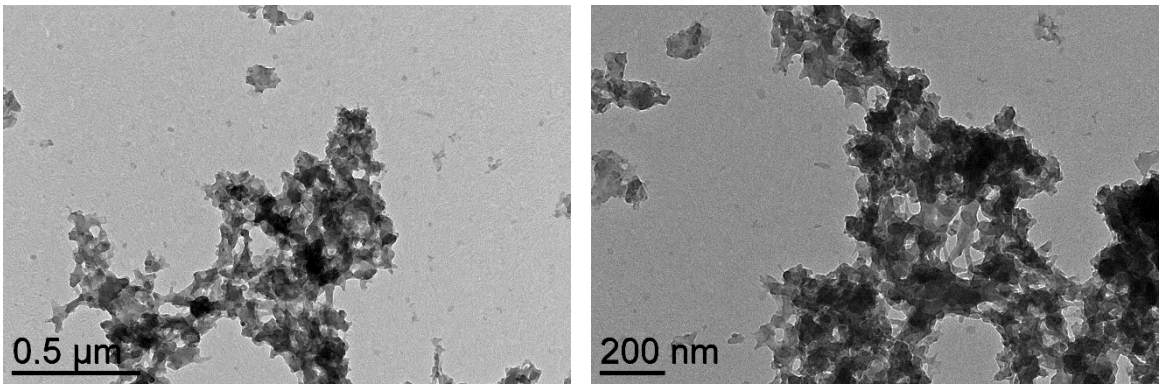


Figure S4.- TEM images of nanoparticles of complex **1** after being suspended in ethanol and heated at 90 °C during 2h

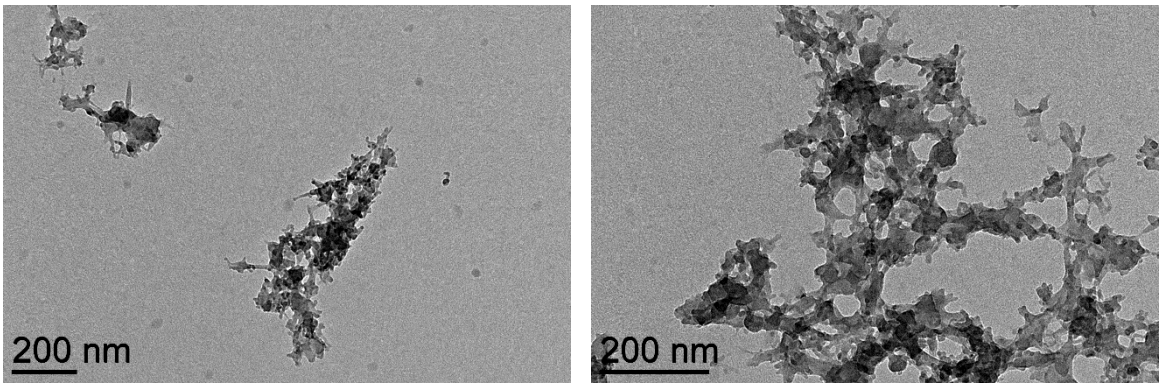


Figure S5.- TEM images of nanoparticles of complex **2** obtained after 20 min of PSM in MW

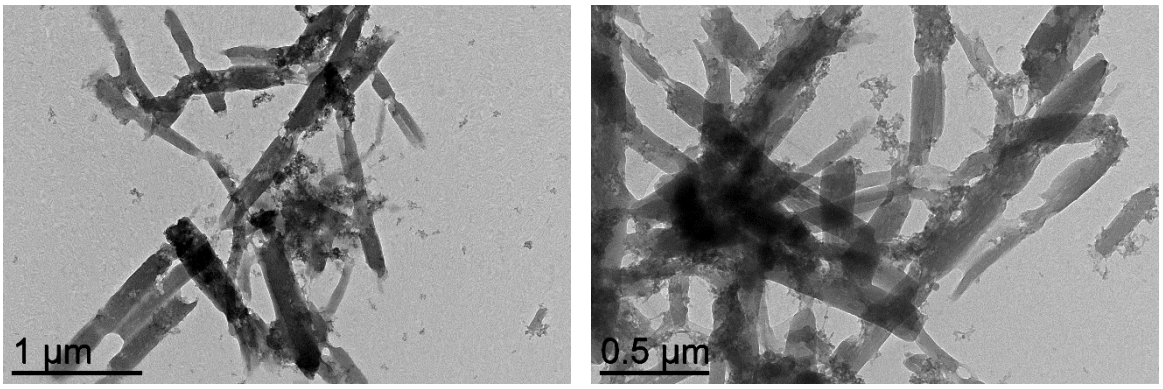


Figure S6.- TEM images of nanoparticles of complex **2** obtained after 30 min of PSM in oil bath

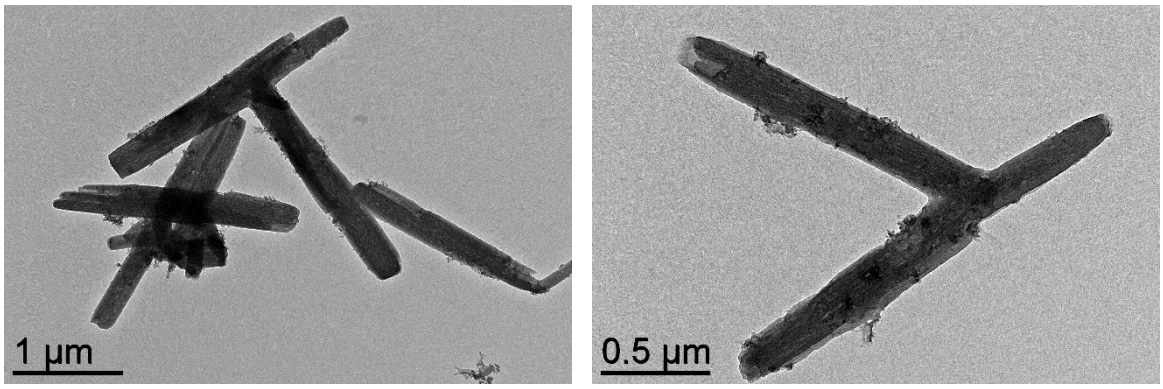


Figure S7.- TEM images of nanoparticles of complex **2** obtained after 1 h of PSM in oil bath

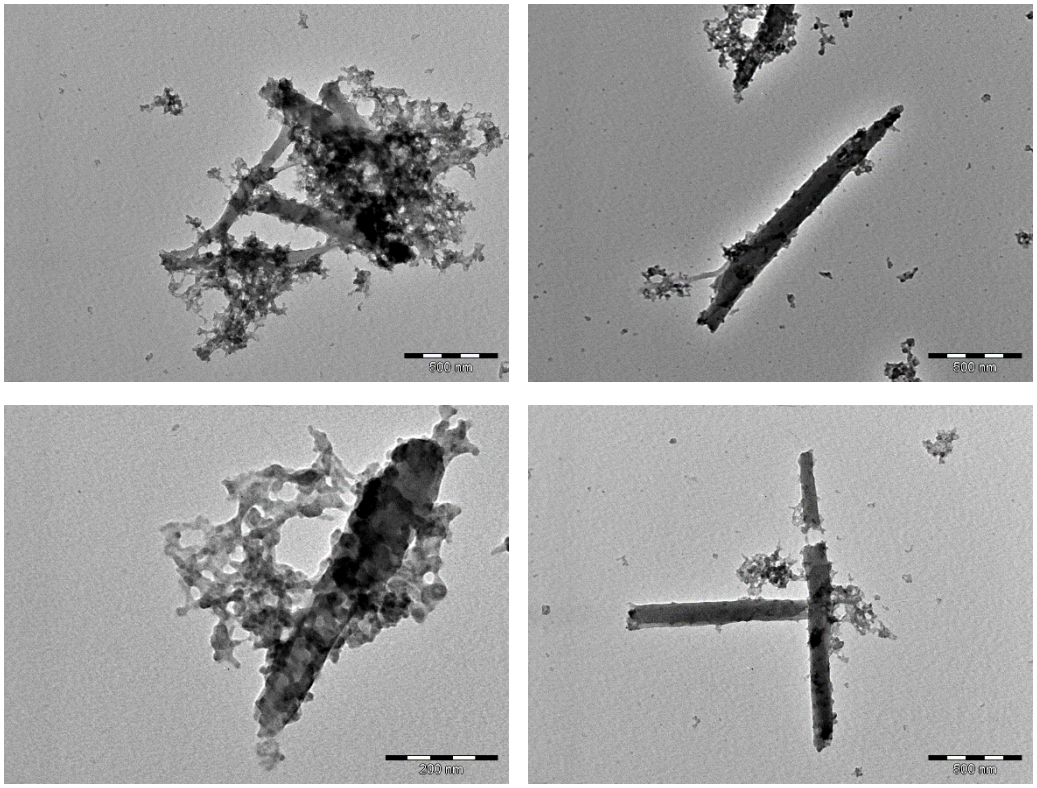
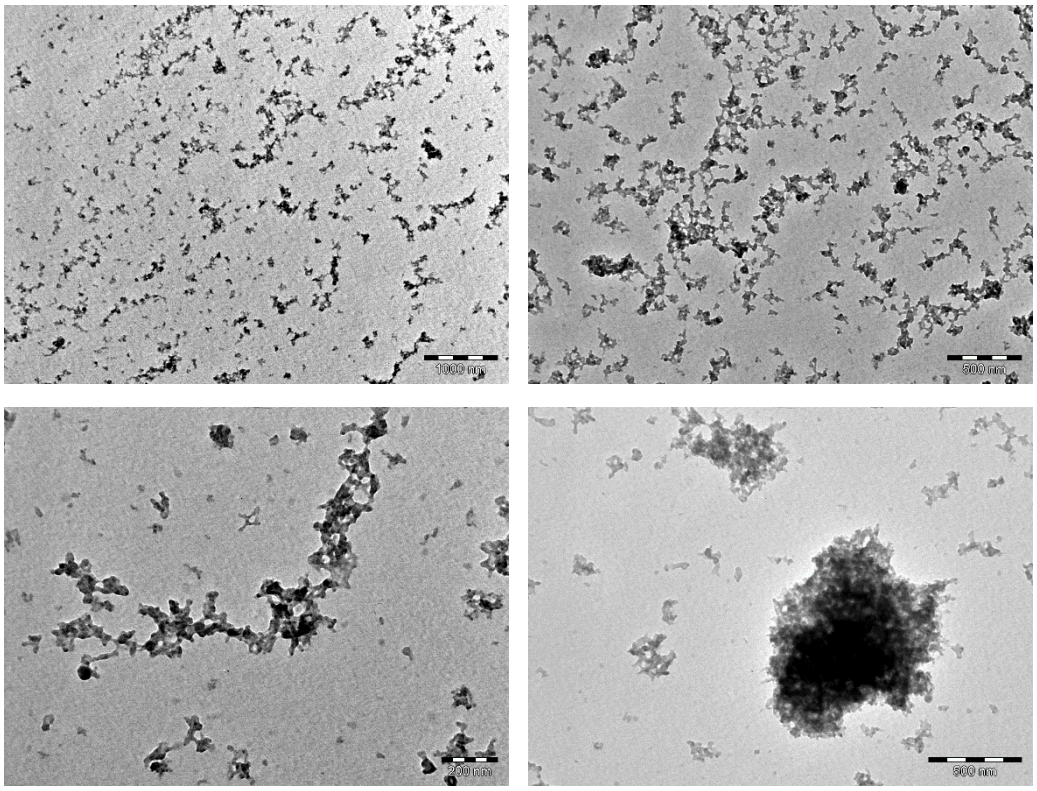


Figure S8.- TEM images of nanoparticles of complex **2** obtained after 2 h of PSM in oil bath



References.

1 A. Enríquez-Cabrera, K. Ridier, L. Salmon, L. Routaboul and A. Bousseksou, *Eur. J. Inorg. Chem.*, 2021, **2021**, 2000–2016.