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Electronic Supporting Information

Versatile Nano-platforms for Hybrid Systems: Revealing Spin-crossover Behavior on Nanoparticles

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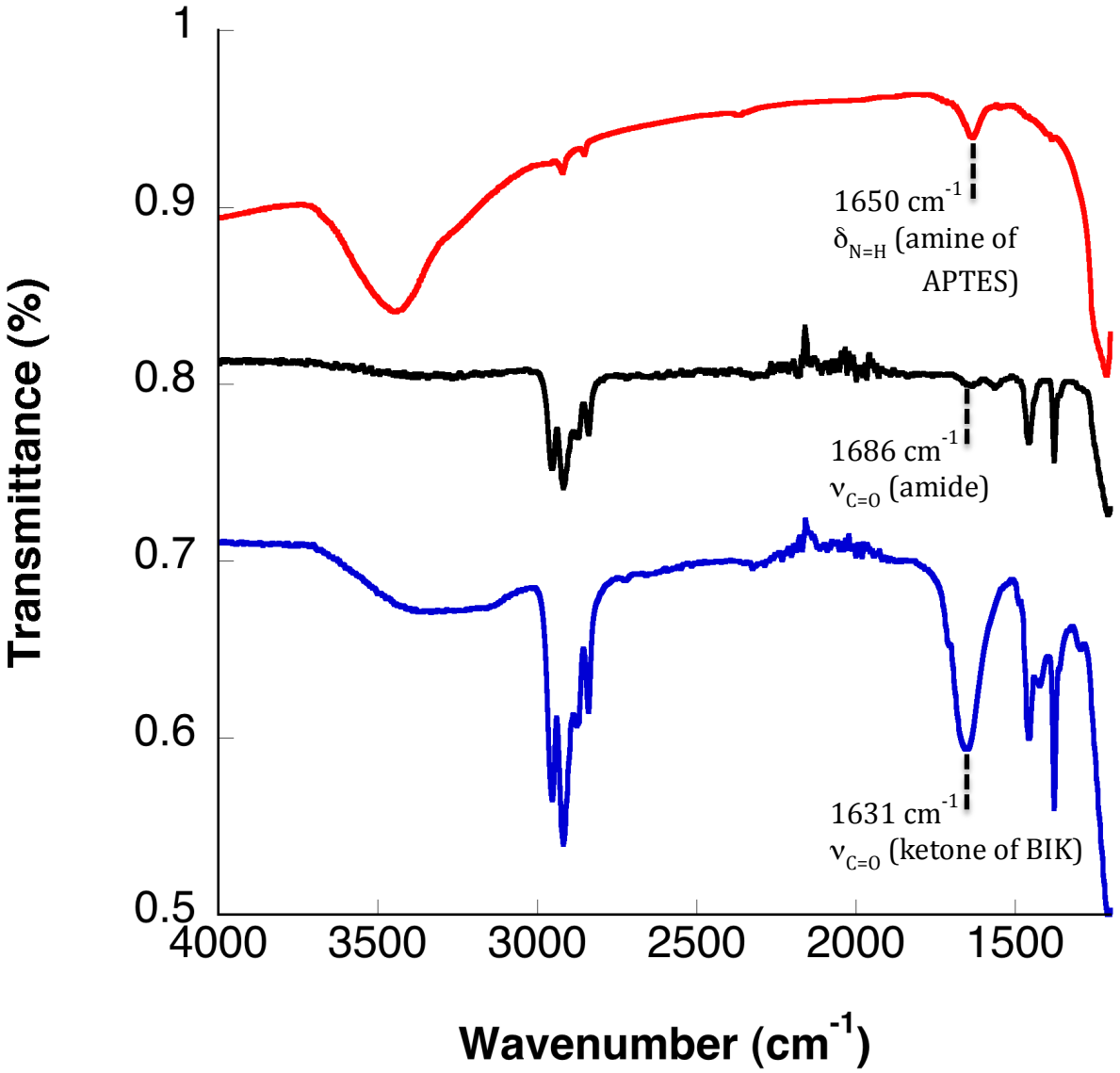
Infra-Red Spectra of the hybrid nanoparticles: APTES-coated silica (red), HBIP-functionalized hybrid (black) and final Fe(II) hybrid (blue).



Estimation of the maximum $\chi_m T$ value for Hybrid Spin-Transition Nanoparticles (HSTNs)

The effective magnetic moment μ_{eff} of a mononuclear complex bearing n unpaired electrons (n = 4 for HS Fe(II)) and a molar magnetic susceptibility χ_M is given by:

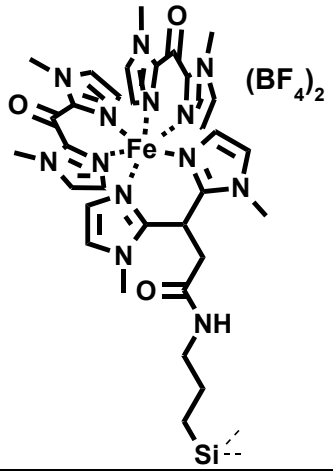
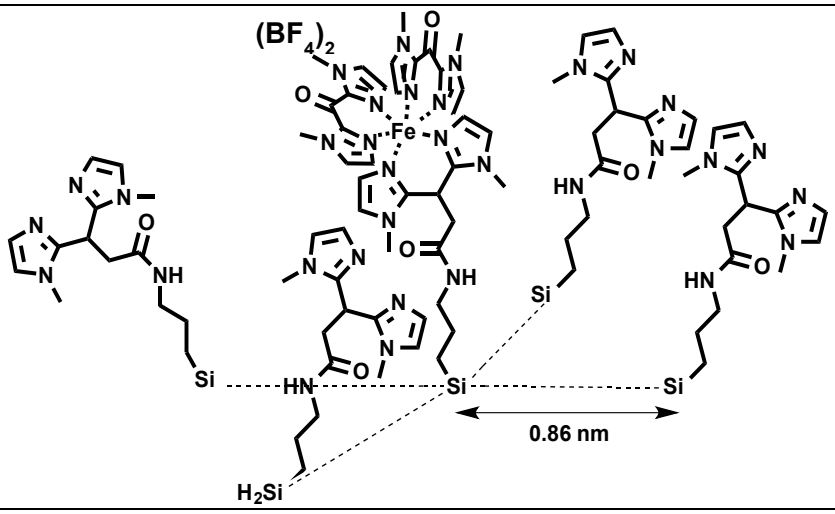
$$\mu_{eff} = \sqrt{n(n+2)} = \frac{\sqrt{3kT\chi_M}}{N\beta} = 2.828\sqrt{\chi_M T}$$

with n = 4, $\mu_{eff} = 4.89\ \mu_B$

and $\chi_M = \frac{(4.89/2.828)^2}{T}$

$\chi_M = 0.01\ emu$ at 300 K

The massic susceptibility χ_m at 300 K is then equal to $\frac{\chi_M}{M}$. The molecular mass of the complex made of the APTES-BIP-Fe-$(BIK)_2$ chain with two tetrafluoroborate as counter ions is M = 977 g.mol^{-1} leading to $\chi_m = 1.10^{-5}\ emu$ and at 300 K, $\chi_m T = 3.10^{-3}\ cm^3.K.g^{-1}$.

Molecular formula of the grafted unit	**Molecular weight**	$\chi_m T$ $cm^3.K.g^{-1}$
	977 g.mol^{-1}	3.10^{-3}
	2181 g.mol^{-1}	$1.3.10^{-3}$

Method for the determination of the amino coverage on the silica cores after the APTES coating

Known masses of approximately 30 mg of the APTES-functionalized particles are reacted with 3.40 mg (10.10^{-6} mol) of N-(9H-fluoren-2-ylmethoxycarbonyloxy)succinimide (FMOC-OSu) in 20 mL of dry DMF and in the presence of Et_3N. The solutions are stirred by ultra-sonication before and during 10 min more after the addition of FMOC-OSu in order to prevent aggregation of the particles. The solid is then separated by centrifugation and the remaining solution of unreacted FMOC-OSu is diluted 10 times before titration by UV-Vis spectroscopy, following the absorbance of the solution at 280 nm. A calibration line has been established using 8 FMOC-OSu solutions ranging from 2.10^{-6} to 70.10^{-6} mol.L^{-1}.

For each aliquot, the number of titrated particles is given by:

$$\frac{m}{mass\ of\ one\ particle} = \frac{m}{volume\ of\ one\ particle \times density} = \frac{m}{{}^{4}/_{3}\,\pi R^3 \times d} \quad (\mathbf{1})$$

with *m* being the mass of particles used for titration, *R* the radius of the particles and *d* the density of silica (2.10^{-21} g.nm^{-3}).

From (**1**), the accessible surface during titration is thus given by:

$$S = surface\ of\ one\ particle \times number\ of\ particles = 4\pi R^2 \times \frac{m}{{}^{4}/_{3}\,\pi R^3 \times d} \quad (\mathbf{2})$$

and at last, the amount of grafted APTES per unit surface is:

$$\boldsymbol{n = \frac{n_{FMOC-OSu}}{S}} \quad (\mathbf{3})$$

with $n_{FMOC\text{-}OSu}$ the amount of reacted FMOC-OSu determined by titration and assuming that the reaction between FMOC-OSu and APTES is quantitative.

From equations (**1**), (**2**) and (**3**), it appears that the parameters to be controlled in order to get an accurate value for *n* are: the exact mass of particles *m* and the radius *R* of the particles. *R* is determined by TEM microscopy. The mass *m* has been corrected after TGA analysis revealing a 10% loss in weight between 28°C and 330°C. This loss is due to a large amount of solvents blocked in the particles because of their porosity.

On a series of 7 titration experiments, with R = 18.4 nm, the amino titration gave:

n = $6.4.10^{-25}$ mol.nm^{-2} (*i.e.* 0.4 amino group/nm^2)