

# SUPPORTING INFORMATION FOR:

## SURFACE PLASMONS REVEAL SPIN CROSSOVER IN NANOMETRIC LAYERS

Gautier Félix,<sup>a</sup> Khaldoun Abdul-Kader,<sup>a</sup> Tarik Mahfoud,<sup>a,b</sup> Il'ya A. Gural'skiy,<sup>a,c</sup> William Nicolazzi,<sup>a</sup> Lionel Salmon,<sup>a</sup> Gábor Molnár,<sup>a,\*</sup> and Azzedine Bousseksou<sup>a,\*</sup>

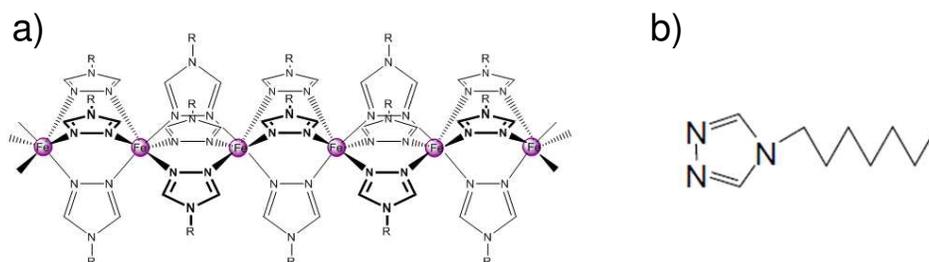
<sup>a</sup> LCC ; CNRS & Université de Toulouse (UPS, INP) ; 205 route de Narbonne, F-31077 Toulouse, France

<sup>b</sup> Optics & Photonics Center (OPC), Moroccan Foundation for Science, Innovation and Research (MAScIR); Technopolis Rabatshore, Morocco

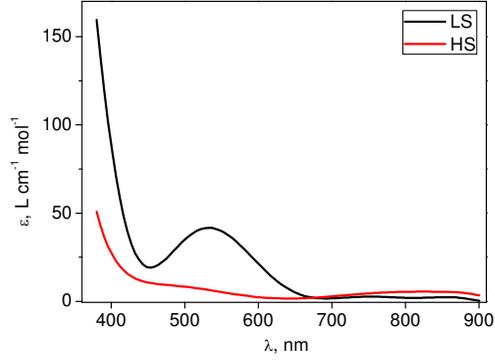
<sup>c</sup> Department of Chemistry, National Taras Shevchenko University, 62 Vladimirska str., 01601 Kiev, Ukraine

### Sample synthesis:

All the chemicals and solvents were obtained from Sigma Aldrich and used without any further purification. 4-heptyl-1,2,4-triazole (figure S1) was prepared from 1-heptylamine, triethyl orthoformate and N-formylhydrazine by a procedure described previously.<sup>1</sup> Iron(II) tosylate hexahydrate was synthesized by reaction between metallic iron and p-toluenesulphonic acid. The solution of the complex  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  was prepared by mixing iron(II) tosylate hexahydrate (30 mg, 0.06 mmol, 1 equiv.) and p-toluenesulphonic acid monohydrate (4 mg, 0.02 mmol) in MeOH (150  $\mu\text{l}$ ) and 4-heptyl-1,2,4-triazole (60 mg, 0.36 mmol, 6 equiv.) in  $\text{CHCl}_3$  (4 ml). The substrates were prepared by depositing 5 nm of titanium and 45 nm of gold on clean glass wafers (BK7 from Schott, 0.5 mm thickness) by means of a Veeco 770 thermal evaporator apparatus at a pressure of  $5 \times 10^{-7}$  mbar. The complex solution (100  $\mu\text{l}$ ) was then spin-coated on this substrate (speed: 4000 rpm, time: 30 s).



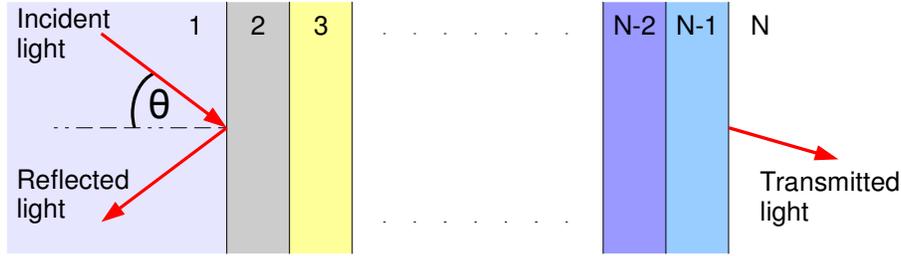
**Figure S1.** (a) Expected chain structure for the triazole family complexes.<sup>2</sup> (b) *hptrz* = 4-heptyl-1,2,4-triazole.



**Figure S2.** Absorption spectra of the  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  complex in the HS and LS states

**Calculation of the refractive index and the HS fraction from the SPR data:**

To determine the complex refractive index and the thickness of the different constituents of our multilayer sample, a fitting with a theoretical curve using the Fresnel equations is required.<sup>3</sup> These equations allow calculating reflected and transmitted light intensity for multi-layers as depicted on Figure S3.



**Figure S3.** Multi-layer representation for reflectivity and transmission analysis.

Each layer is characterized by a matrix  $M_k$ , displayed in equation (2), which allows calculating the matrix  $M$  of the multi-layer system as shown in equation (1).

$$M = \prod_{k=2}^{N-1} M_k \quad (1)$$

$$M_k = \begin{pmatrix} \cos(\beta_k) & \frac{-i \sin(\beta_k)}{q_k} \\ -i q_k \sin(\beta_k) & \cos(\beta_k) \end{pmatrix} \quad (2)$$

with,  $q_k = \frac{(\varepsilon_k - n_1^2 \sin^2(\theta_1))^{1/2}}{\varepsilon_k}$ ,  $\beta_k = \frac{2\pi d_k}{\lambda} (\varepsilon_k - n_1^2 \sin^2(\theta_1))^{1/2}$ ,  $\varepsilon_k = n_k^2$

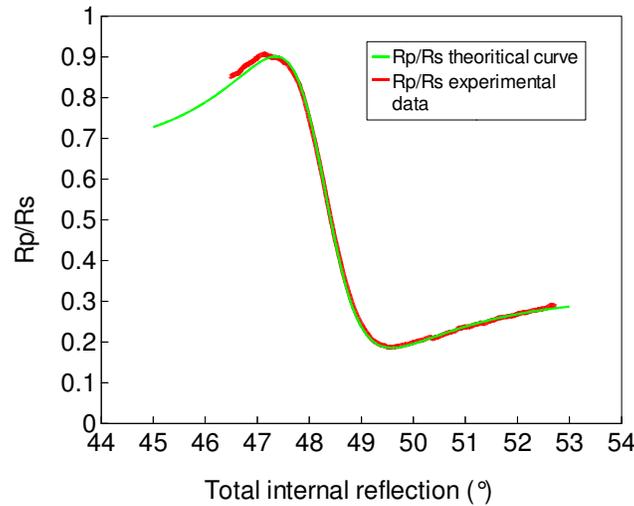
The amplitude reflection coefficient for p-polarized light ( $r_p$ ) is calculated with these matrix elements as:

$$r_p = \frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \quad (3)$$

Then, the intensity reflection coefficient for p-polarized light ( $R_p$ ) can be obtained by:

$$R_p = |r_p|^2 \quad (4)$$

Figure S4 shows an example for fitting the experimental data by this method. The fitting allows also a more complete characterization of the sample: the thickness of titanium, gold and  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  can be extracted additionally to the  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  refractive index.



**Figure S4.** Fitting of an experimental curve at  $T = 293 \text{ K}$  and  $\lambda = 660 \text{ nm}$  by a theoretical curve calculated with the Fresnel equations. The theoretical curve is obtained for the multi-layer glass/ Ti (22.5 nm)/ Au (40.5 nm)/  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  (29.8 nm) with a complex refractive index of  $n^* = 1.585 + 0.0055 i$  for  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$ .

Using this approach one can convert the  $\theta_{\text{SPR}} = f(T)$  data into  $n = f(T)$  curves. To simplify this conversion two approximations were made: (1) Thickness and refractive index variations of titanium, gold and glass are neglected. (2) The variation of the thickness of the  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  film is supposed to be negligible as well. The first approximation is well supported by the experimental data shown in the manuscript (Figure 1). The latter approximation is, however, rather crude because even very small thickness variations (less than 1 %) are detectable and the spin state change may involve a change of the crystal unit cell parameters up to 5–10 %.<sup>2,4</sup> Therefore the calculated refractive index values (Figure S5(a)) should be considered as “effective values”. To calculate the accurate values of  $n$  the sample thickness should be determined at each temperature by AFM. One should also note that the refractive index of this material is

anisotropic, but the thin films are not oriented (*i.e.* not single crystalline) therefore what we determine from the SPR experiments is a mean value for  $n$ .

In the last step, we have determined the high spin and low spin fractions ( $\gamma_{HS} + \gamma_{LS} = 1$ ) from the refractive index values as a function of the temperature using the Maxwell-Garnett equation:

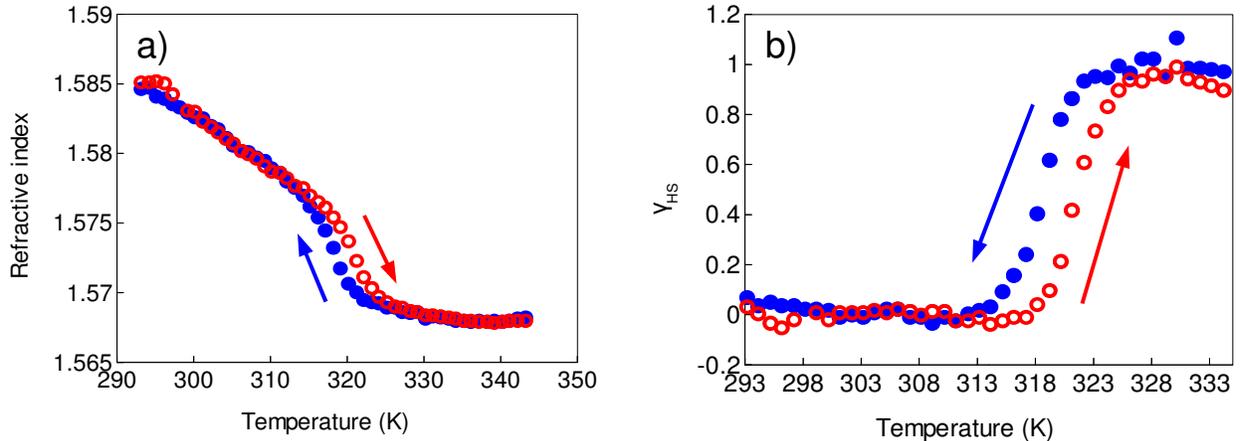
$$\frac{\epsilon_{eff} - \epsilon_m}{\epsilon_{eff} + 2\epsilon_m} = q_i \frac{\epsilon_i - \epsilon_m}{\epsilon_i + 2\epsilon_m} \quad (5)$$

where  $n = \sqrt{\epsilon}$

This equation allows calculating an effective refractive index of a material with impurities ( $\epsilon_{eff}$ ), if the volume fraction of the impurities ( $q_i$ ) and the refraction indexes of the material ( $\epsilon_m$ ) and impurities ( $\epsilon_i$ ) are known. This relation works only if the size of the impurities is lower than the wavelength of the light.<sup>5</sup> In our case we consider that the whole material is in the LS state at 293 K and in the HS state at 340 K. During the warming the HS state will be considered as an impurity. This approximation leads to equation (6), from which we obtain equation (7) for the HS fraction. Figure S5(b) displays the calculated  $\gamma_{HS}(T)$  curve. Strictly speaking this approach is valid only in the case of homogeneous phase transformations. Further work will be necessary using extended Maxwell-Garnett theories in order to take into account the phase separation.<sup>6</sup>

$$\frac{\epsilon_{eff} - \epsilon_{BS}}{\epsilon_{eff} + 2\epsilon_{BS}} = \gamma_{HS} \frac{\epsilon_{HS} - \epsilon_{BS}}{\epsilon_{HS} + 2\epsilon_{BS}} \quad (6)$$

$$\gamma_{HS} = \frac{\epsilon_{eff} - \epsilon_{BS}}{\epsilon_{eff} + 2\epsilon_{BS}} \frac{\epsilon_{HS} + 2\epsilon_{BS}}{\epsilon_{HS} - \epsilon_{BS}} \quad (7)$$



**Figure S5.** (a) Thermal variation of the refractive index for a glass/ Ti (5 nm)/ Au (45 nm)/ [Fe(hptrz)<sub>3</sub>](OTs)<sub>2</sub> (30 nm) multi-layer calculated by fitting the experimental SPR data shown in figure 3. (b) Conversion of the refractive index into HS fraction using the Maxwell-Garnett equation.

**Effect of the film thickness change on the SPR signal:**

The plasmon resonance angle localization depends both on the thickness and on the refractive index of the SCO material. With increasing temperature the refractive index  $n$  will decrease, while the sample thickness  $h$  will increase. This leads to opposing effects on the plasmon resonance angle. Figure 3(b) of the article shows that the SPR angle decreases with the temperature in the whole measurement range. This means that the refractive index variation has a more important influence than the thickness change. Using the empirical Gladstone-Dale relationship<sup>7</sup> (eq. 8) we can explain this observation as follows:

$$n = 1 + r \frac{m}{V} \quad (8)$$

where,  $n$ : refractive index,  $r$ : constant,  $m$ : mass,  $V$ : volume. From this one can deduce that:

$$\frac{\Delta V}{V} = \frac{\Delta n}{1-n} \quad (9)$$

If the volume variation of the film is isotropic, the variation of the thickness  $h$  can be linked to the variation of the volume by:

$$\frac{\Delta h}{h} = \sqrt[3]{\frac{\Delta V}{V} + 1} - 1 \approx \frac{\Delta V}{3V} \quad (\text{for } \Delta V \ll V) \quad (10)$$

With these approximations and if  $n > 1.5$  we obtain:

$$\left| \frac{\Delta n}{n} \right| > \left| \frac{\Delta h}{h} \right| \quad (11)$$

The refractive index of [Fe(hptrz)<sub>3</sub>](OTs)<sub>2</sub> is higher than 1.5, hence we can conclude that the relative variation of the refractive index will be more important than that of the thickness - in agreement with the experimental observations.

**Temperature effect on the refractive index:**

The refractive index variation with the temperature is mainly due to a thermal expansion of the material (far from the spin transition temperature). Thermal variation of

refractive index can be analyzed with the Debye model in the quasi-harmonic approximation.<sup>8</sup> We can consider the phonon dispersion relations of the low and high temperature phases:

$$\omega_i = \frac{k_i c}{n_i}, \text{ with } k_i = \frac{2\pi}{(V_i)^{1/3}} \quad (12)$$

where  $i$  indicates the HS or LS phase,  $\omega_i$  is the angular momentum,  $k_i$  the corresponding wave vector,  $c$  the velocity of light,  $n_i$  the refractive index and  $V_i$  the volume of the phase  $i$ .

We can write the total derivative of the refractive index as:

$$dn_i = \frac{c}{\omega_i} dk_i - \frac{k_i c}{\omega_i^2} d\omega_i \quad (13)$$

In the quasi-harmonic approximation, the angular momentum  $\omega_i$  is supposed to be volume dependent through the Grüneisen parameter  $\gamma_i$ :

$$\gamma_i = \frac{\partial \ln \omega_i}{\partial \ln V_i} = \frac{3B_i \alpha_i}{C_{v,i}} \quad (14)$$

where  $B_i$ ,  $\alpha_i$  and  $C_{v,i}$  stand for the bulk modulus, **the thermal expansion coefficient** and the specific heat of the solid, respectively. From the precedent equations a relationship between the refractive index  $n_i$  and the temperature can be easily established:

$$n_i(T) = n_0 \exp \left[ -\alpha_i \left( \frac{2\pi}{3} - \gamma_i \right) (T - T_0) \right] \quad (15)$$

where  $n_0$  and  $T_0$  correspond to the reference refractive index and temperature, respectively, chosen far from the transition temperature. **Since the thermal expansion coefficient is small and constant over our experimental temperature range**, a Taylor expansion of  $n_i(T)$  can be performed and we finally obtain:

$$n_i(T) \approx n_0 - \alpha_i \left( \frac{2\pi}{3} - \gamma_i \right) (T - T_0) \quad (16)$$

This equation reproduces the experimentally observed linear relationship between the temperature and the optical properties ( $n$  or  $\theta_{SPR}$ ). Equation (16) shows also that the slope of the  $\theta_{SPR}(T)$  curves in the HS and LS phases (far from the spin state change) are different - in agreement with the experimental findings. It would be very useful to determine the thermal expansion coefficient of  $[\text{Fe}(\text{hptrz})_3](\text{OTs})_2$  in the HS and LS

phases (for example using X-ray diffraction) in order to quantitatively connect it to the SPR shift.

**References:**

- (1) Bayer, H. O.; Cook, R. S.; von Mayer, W. C. *US Patent* **1974**, 3821376.
- (2) Urakawa, A.; Beek, W. V.; Monrabal-Capilla, M.; Galán-Mascarós, J. R.; Palin, L.; Milanesio M. *J. Phys. Chem. C* **2011**, *115*, 1323-1329.
- (3) Gupta, B.D.; Sharma, A.K. *Sens. Act. B* **2005**, *107*, 40-46.
- (4) (a) Halcrow, M.A. *Chem. Soc. Rev.* **2011**, *40*, 4119-4142. (b) Guionneau, P.; Marchivie, M.; Bravic, G.; Létard, J.-F.; Chasseau, D. *Top. Curr. Chem.* **2004**, *234*, 97-128.
- (5) Maxwell Garnett, J. C. *Phil. Trans. R. Soc. Lond. A* **1904**, *203*, 385-420.
- (6) Ruppin, R. *Opt. Comm.* **2000**, *182*, 273-279.
- (7) (a) Gladstone, J. H.; Dale, T. P. *Phil. Trans. R. Soc. Lond.* **1863**, *153*, 317-343. (b) Teertstra, D. K. *Can. Mineral.* **2005**, *43*, 543-552.
- (8) Kittel, C. *Introduction to Solid State Physics*, 7th Ed., Wiley, (1996)