Electronic Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2021

Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2021

## **Supporting Information File**

# Wet-Chemistry Assembly of One-Dimensional Nanowires: Switching Characteristics of a Known Spin-Crossover Iron(II) Complex Through Raman Spectroscopy

Zoi G. Lada, Athanassios Chrissanthopoulos, Spyros P. Perlepes, Konstantinos S. Andrikopoulos and George A. Voyiatzis

**Abstract:** In this study, a simple, fast, one-pot approach for the isolation of nanowires (NWs) in coordination chemistry is reported. Nanowires (NWs) of spin-crossover (SCO) materials are extremely rare. Here, an innovative and easy synthetic process was developed to prepare NWs of a switchable polymorph of the known complex *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] using a wet-chemistry approach for the first time; abpt is the bidentate chelating ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole. The remarkable smooth of the high-spin to low-spin transition, monitored through variable-temperature (300-80 K) Raman microscopy compared with the sharp transition exhibited by the polycrystalline material, demonstrates the effect of the topological properties on the physical phenomena of the system.

## **Table of Contents**

EXPERIMENTAL SECTION	
Materials and Characterization Techniques	3
Preparation of <i>trans</i> -[Fe(NCS) <sub>2</sub> (abpt) <sub>2</sub> ]	
(Polymorph A) Nanowires (~100 nm diameter)	3
Computational Details	3
DIAGNOSTIC RESULTS AND BRIEF DISCUSSION	
Synthesis Comments	3
Structural Features	4
Spectroscopic Features	4
Computational Studies	6
Reduced Raman Representation	10
REFERENCES	11

#### LIST OF TABLES

Table S1. Calculated Fe<sup>II</sup>-N bond lengths at the optimized structures of the LS and HS forms of the polymorph **A** of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (atoms' numbering as in Figs S6 and S7, respectively), along with the experimental ones at 120 and 270 K. Calculations have been performed at the CAM-B3LYP/Pvdz level of theory. **Table S2.** Atoms' cartesian coordinates at equilibrium geometry of the Low-Spin (LS) form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**). **Theory/basis set:** CAM-B3LYP/pVDZ.

Table S3. Atoms' cartesian coordinates at equilibrium geometry of the High-Spin (HS) form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A). Theory/basis set: CAM-B3LYP/pVDZ.

#### LIST OF FIGURES

**Fig. S1.** (a) The formation of intermolecular H bonds in the 270 K crystal structure of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**) with the S atoms of the isothiocyanato groups as acceptors and the -NH<sub>2</sub> groups of the two neighbouring molecules as donors. (b) Portions of three chains in the network of the complex emphasizing the formation of the intermolecular HNH<sup>...</sup>S H bonds. The pictures have been created from the .cif of the structure deposited in the CCDC.<sup>7,8</sup>

Fig. S2. Diameter distribution of the polymorph A NWs of trans-[Fe(NCS)2(abpt)2].

Fig. S3. Raman spectra of the non-SCO form (polymorph B) and the SCO form (polymorph A) of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] at room-temperature and at 83 K.

**Fig. S4.** (a) Room-temperature UV-Vis spectrum of an acetone suspension of the pink NWs of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>]. The absorption band with a maximum at ~500 nm results from a charge transfer process within the complex and it is responsible for its macroscopic color. The UV/Vis spectrum of the suspension is identical to the room-temperature UV/Vis spectrum of an acetone suspension of powdered single crystals of the polymorph **A**. (b) Room-temperature ATR spectra of the free organic ligand abpt and the pink NWs of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>]. The high-frequency shifts of the vibrational abpt modes in the spectrum of the complex compared to those of the free ligand and the appearance of the isothiocyanato  $v(C\equiv N)$  band at 2083 cm<sup>-1</sup> are both indicative of complex formation. The ATR spectrum of the NWs of the complex is identical to the room-temperature spectrum of a powdered sample of the single crystals of polymorph **A**.

Fig. S5. Room-temperature Raman spectra of the pink NWs of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] and the free organic ligand. The spectrum of the NWs of the complex is identical to the room-temperature spectrum of a powdered sample of single crystals of the polymorph **A**.

Fig. S6. In situ temperature dependent Raman spectra of NWs of the polymorph A of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] in the 140-2200 cm<sup>-1</sup> region.

Fig. S7. Ball and stick drawing of the optimized structure of the Low-Spin (LS) form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A) (atoms' numbering as in Table S2).

**Fig. S8**. Ball and stick drawing of the optimized structure of the High-Spin (HS) form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**) (atoms' numbering as in **Table S3**). **Fig. S9**. Calculated unscaled (a) low- and (b) high-frequency Raman spectra of the LS and HS forms of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**) [Raman activity in Å<sup>4</sup>.(amu)<sup>1</sup>]. Calculations have been performed at the optimized geometries at the CAM-B3LYP/pVDZ level of theory.

**Fig. S10**. Effect of the *Reduced Raman Procedure* on the calculated HS<sup>R</sup> values for two pairs of vibrational peaks, associated with the HS and LS species of the polymorph **A** of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>]. (a) The peaks are of comparable energy (2128 cm<sup>-1</sup> and 2090 cm<sup>-1</sup>); (b) The peaks have a significant energy difference (165 cm<sup>-1</sup> and 2090 cm<sup>-1</sup>).

Page

### **Experimental Section**

**Materials and Characterization Techniques**. All manipulations were performed under a nitrogen atmosphere, using materials (reagent grade) and solvents as received. The ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (abpt) is commercially available (Aldrich). Elemental analyses (C, H, N) were performed by the University of Patras microanalytical service using a Perkin Elmer 2400 analyzer. FT-IR spectra were recorded in the solid state on a Bruker FT-IR spectrometer Equinox 55 equipped with an ATR accessory of Pike Technologies and spectral resolution 4 cm<sup>-1</sup>. UV/Vis spectra were recorded on a Hitachi U-3000 spectrometer. The morphology of the samples was evaluated from the scanning electron microscope (SEM) images. The instrument used was Zeiss ZUPRA 35 VP-FEG, operating at 5-20 KeV. Raman spectra were recorded using the Horiba-JY T-64000 micro-Raman system. The excitation wavelength was 632.8 nm (HeNe laser, Optronics Technologies S.A., model HLA-20P, 20 mW), while the power on the sample was set to 1 mW. Backscattering geometry from a long working distance microscope objective (50x, NA: 0.55) was selected and the scattered photons were detected from a liquid nitrogen cooled 2D-CCD detector after being dispersed by a single monochromator (equipped with a 600 grooves/mm grating). The spectral resolution was ~3.5 cm<sup>-1</sup>. The Rayleigh scattered photons were rejected by an appropriate Edge filter. The calibration of the instrument was initially carried out using the standard Si Raman peak position at 520.5 cm<sup>-1</sup> and additionally based on the Ne lamp spectrum regularly obtained in the spectral windows of interest. Low temperature Raman spectra were collected *in situ* by using a temperature-controlled stage, THMS600/720, which enables the stabilization of temperature at the desired value in the 80-870 K range with a precision better than ±0.5 K.

**Preparation of** *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (Polymorph A) Nanowires (~100 nm diameter). Me<sub>2</sub>CO (10 mL) was bubbled with N<sub>2</sub> in a round-bottom flask for approximately 30 min and then solid FeSO<sub>4</sub>·7H<sub>2</sub>O (36.14 mg, 0.13 mmol) was added resulting in a pale greenish solution. A colorless solution of KSCN (24.3 mg, 0.25 mmol) in Me<sub>2</sub>CO (5 mL) was then added to the previous solution under stirring. Immediate precipitation of a colorless solid (K<sub>2</sub>SO<sub>4</sub>) was observed. The precipitate was removed by filtration and a colorless solution of abpt (59.56 mg, 0.25 mmol) in MeOH (5 mL) was added to the filtrate giving an orange-red solution. This solution was intensely stirred (800-1000 rpm) for 25 min under N<sub>2</sub>, during which time a purple-pink solid was precipitated. The solid was collected by filtration, washed with cold MeOH (2x0.5 mL) and Et<sub>2</sub>O (2x2 mL), and dried *in vacuo* under N<sub>2</sub> for 3 hours. Typical yields were in the 25-30% range. Anal. Calcd for C<sub>26</sub>H<sub>20</sub>N<sub>14</sub>S<sub>2</sub>Fe: C, 48.15; H, 3.11; N, 30.24. Found: C, 48.58; H, 3.05; N, 30.64%.

**Computational Details.** *Methods and basis sets:* The CAM-B3LYP hybrid density functional approach <sup>1-4</sup> was employed as implemented in the GAUSSIAN 09 program package.<sup>5</sup> This method is an exchange-correlation functional with short and long-range correction. All-electron, fully optimized contracted Gaussian-basis sets of double-*ζ* valence quality (Ahlrichs pVDZ)<sup>6</sup> have been used for calculations. *Structural methods*: The geometries of the High-Spin (HS) and Low-Spin (LS) molecular models have been fully optimized using the Berny algorithm. In order to have a more realistic study of the crystal structure and intermolecular interactions, two NH<sub>3</sub> molecules have been added in our structural models in between specific groups (-NH<sub>2</sub>…NH<sub>3</sub>…SCN-), see Figs. S7 and S8. Calculated and experimental Fe-N bond lengths are listed in Table S1. *Vibrational properties*: All optimized geometries (Tables S2 and S3) are characterized as stationary points on the potential energy surface with vibrational frequency calculations. Harmonic vibrational frequencies, IR intensities and Raman activities of the LS and HS states have been calculated at the CAM-B3LYP/pVDZ level of theory (Fig. S9, Videos S1-S10).

## Main Text Paragraph.

### **Diagnostic Results and Brief Discussion**

Synthesis Comments. The preparation of the complex is represented by the chemical equation (1).

$$FeSO_4.7H_2O + 2 KSCN + 2 abpt \xrightarrow{Me_2CO/MeOH} trans- [Fe(NCS)_2(abpt)_2] + K_2SO_4 + 7 H_2O \quad (1)$$

The solvent mixture used, the volume ratio (Me<sub>2</sub>CO:MeOH= 3:1), the concentration of the reactants in the reaction system and the stirring time are all crucial factors for the isolation of NWs.

Another important factor is the addition of abpt in the last step of the procedure, i.e. after the removal of K<sub>2</sub>SO<sub>4</sub>.

**Structural Features.** 



**Fig. S1.** (a) The formation of intermolecular H bonds in the 270 K crystal structure of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**) with the S atoms of the isothiocyanato groups as acceptors and the -NH<sub>2</sub> groups of the two neighbouring molecules as donors. (b) Portions of three chains in the network of the complex emphasizing the formation of the intermolecular HNH···S H bonds. The pictures have been created from the cif of the structure deposited in the CCDC.<sup>7,8</sup>

#### Statistical Analysis.



Fig. S2. Diameter distribution of the polymorph A NWs of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>].

#### Spectroscopic Features.



Fig. S3. Raman spectra of the non-SCO form (polymorph B) and the SCO form (polymorph A) of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] at room-temperature and at 83 K.



**Fig. S4.** (a) Room-temperature UV-Vis spectrum of an acetone suspension of the pink NWs of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>]. The absorption band with a maximum at ~500 nm results from a charge-transfer process within the complex and it is responsible for its macroscopic color. The UV/Vis spectrum of the suspension is identical to the room-temperature UV/Vis spectrum of an acetone suspension of powdered single crystals of the polymorph **A**. (b) Room-temperature ATR spectra of the free organic ligand abpt and the pink NWs of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>]. The high-frequency shifts of the vibrational abpt modes in the spectrum of the complex compared to those of the free ligand and the appearance of the isothiocyanato v(C=N) band at 2083 cm<sup>-1</sup> are both indicative of complex formation. The ATR/FT-IR spectrum of the NWs of the complex is identical to the room-temperature spectrum of a powdered sample of the single crystals of polymorph **A**.



Fig. S5. Room-temperature Raman spectra of the pink NWs of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] and the free organic ligand. The spectrum of the NWs of the complex is identical to the room-temperature spectrum of a powdered sample of single crystals of the polymorph **A**.



Fig. S6. In situ temperature-dependent Raman spectra of NWs of the polymorph A of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] in the 140-2200 cm<sup>-1</sup> region.

We have introduced the proportionality constant K in order to compensate for the Raman cross-section difference of the two vibrational modes. The value of K is derived by taking into account the integrated intensity of the two peaks at 81 K and 298 K in which LS and HS population, respectively, is equal to 1. For each pair of bands, the K value may differ and is therefore calculated each time. This type of normalization could be exploited in other systems as well, in order to compensate for the alterations of Raman cross-sections in different vibrational scattering modes, leading to the calculation of the HS and LS populations via Raman spectroscopy.

**Computational Studies.** The DFT model structures associated with the LS and HS states of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**) are presented in Figs. S7 and S8. The model includes two NH<sub>3</sub> molecules as described in the "Computational Details" part of the EXPERIMENTAL SECTION, and enables the calculation of iron(II)-donor atom bond lengths which are expected to be different for the HS and LS forms. The experimental values related to the Fe<sup>II</sup>-N distances at two characteristic temperatures, i.e. at 120 K describing the LS state<sup>7,9</sup> and at 270 K describing the HS state, <sup>7,8</sup> are listed in Table S1 along with the calculated ones.



Fig. S7. Ball and stick drawing of the optimized structure of the Low-Spin (LS) form of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A) (atoms' numbering as in Table S2).



Fig. S8. Ball and stick drawing of the optimized structure of the High-Spin (HS) form of trans-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A) (atoms' numbering as in Table S3).

Table S1. Calculated Fe<sup>II</sup>-N bond lengths at the optimized structures of the LS and HS forms of the polymorph A of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (atoms' numbering as in Figs S7 and S8, respectively), along with the experimental ones at 120 and 270 K. Calculations have been performed at the CAM-B3LYP/Pvdz level of theory.

	LS		нѕ	
	calcd	exp (120 K) <sup>[a]</sup>	calcd	exp (270 K) <sup>[b]</sup>
Fe1-N1, Fe1-N34	1.963	1.953	2.105	2.131
Fe1-N5, Fe1-N36	2.011	1.955	2.199	2.134
Fe1-N4, Fe1-N35	2.029	2.007	2.220	2.215

[a] From refs. 7 and 9.

[b] From refs. 7 and 8.

It is evident that the experimental three Fe<sup>II</sup>-N bond lengths of the LS form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph **A**) experience a reduction of ~10% compared to the corresponding distances of the HS form of the complex. The calculated (DFT) bond lengths follow the same trend.

Table S2. Atoms' cartesian coordinates at equilibrium geometry of the Low-Spin (LS) form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A). Theory/basis set: CAM-B3LYP/pVDZ.

= 0 Multiplicity	= 1	
0.0246270924	0.0163492039	0.0201808418
-1.3787896110	0.9310798994	-4.3980212654
-0.5092805344	0.7088745485	-1.7369485576
1.8546056702	0.8807773567	-0.1298588356
-0.3438639803	1.7463475580	0.9768448799
-1.3490539193	2.3024755902	1.6564030121
0.4778043043	3.4531352694	2.0435813481
1.4271652447	4.3046097113	2.5999430616
1.8324452796	3.7724803343	3.4071195951
0.9017799123	5.1059917228	2.9564202217
-1.0593336666	5.3463490694	3.6091611592
-0.8709155990	0.8127362991	-2.8455091217
2.8967545977	0.3943107716	-0.7986902842
2.7324773724	-0.5536766121	-1.3148776139
4.1275412537	1.0454742488	-0.8263373284
4.9543039007	0.6088872780	-1.3880006049
4.2764044426	2.2395677235	-0.1331698357
5.2290803496	2.7728759787	-0.1384081095
3.1929036549	2.7507475931	0.5730598899
3.2403780170	3.6807313660	1.1376635332
1.9986583954	2.0378837686	0.5438633637
0.7560734381	2.4421271493	1.1913711688
-0.8590445671	3.3327197318	2.3133228509
-1.6460440135	4.2298838566	3.1703885017
	<pre>= 0 Multiplicity 0.0246270924 -1.3787896110 -0.5092805344 1.8546056702 -0.3438639803 -1.3490539193 0.4778043043 1.4271652447 1.8324452796 0.9017799123 -1.059336666 -0.8709155990 2.8967545977 2.7324773724 4.1275412537 4.9543039007 4.2764044426 5.2290803496 3.1929036549 3.2403780170 1.9986583954 0.7560734381 -0.8590445671 -1.6460440135</pre>	<pre>= 0 Multiplicity = 1 0.0246270924 0.0163492039 -1.3787896110 0.9310798994 -0.5092805344 0.7088745485 1.8546056702 0.8807773567 -0.3438639803 1.7463475580 -1.3490539193 2.3024755902 0.4778043043 3.4531352694 1.4271652447 4.3046097113 1.8324452796 3.7724803343 0.9017799123 5.1059917228 -1.0593336666 5.3463490694 -0.8709155990 0.8127362991 2.8967545977 0.3943107716 2.7324773724 -0.5536766121 4.1275412537 1.0454742488 4.9543039007 0.6088872780 4.2764044426 2.2395677235 5.2290803496 2.7728759787 3.1929036549 2.7507475931 3.2403780170 3.6807313660 1.9986583954 2.0378837686 0.7560734381 2.4421271493 -0.8590445671 3.3327197318 -1.6460440135 4.2298838566</pre>

С	-1.7602773253	6.1760233424	4.3759293088
Н	-1.2436088203	7.0794333975	4.7149520325
С	-3.0806214913	5.9387770020	4.7417255693
Н	-3.6137925128	6.6516953799	5.3723365242
С	-3.6935429196	4.7757077285	4.2816498246
Н	-4.7291200263	4.5509930105	4.5451890641
С	-2.9698579965	3.9026755710	3.4834522825
Н	-3.3994563786	2.9795804885	3.0965521517
S	1.4277675490	-0.8983370663	4.4384781484
Ν	0.5585290425	-0.6761718825	1.7773135278
Ν	-1.8053507844	-0.8480768289	0.1702183020
Ν	0.3931191217	-1.7136492308	-0.9364827253
Ν	1.3983099223	-2.2697781564	-1.6160394079
Ν	-0.4285483902	-3.4204373995	-2.0032185059
Ν	-1.3779079657	-4.2719132366	-2.5595794722
Н	-1.7831690998	-3.7397960270	-3.3667738440
Н	-0.8525234798	-5.0733044098	-2.9160367475
Ν	1.1085968506	-5.3136611389	-3.5687830700
С	0.9200538085	-0.7800142745	2.8859117642
С	-2.8475013629	-0.3616067076	0.8390447425
Н	-2.6832234537	0.5863797208	1.3552335942
С	-4.0782902635	-1.0127661222	0.8666854903
Н	-4.9050542264	-0.5761763729	1.4283446359
С	-4.2271542242	-2.2068589888	0.1735172127
Н	-5.1798322093	-2.7401635280	0.1787504134
С	-3.1436517771	-2.7180423961	-0.5327073323
Н	-3.1911264810	-3.6480253330	-1.0973122417
С	-1.9494045608	-2.0051823441	-0.5035051927
С	-0.7068184427	-2.4094279185	-1.1510096858
С	0.9083011430	-3.3000231413	-2.2729581657
С	1.6953031682	-4.1971906482	-3.1300183664
С	1.8095433021	-6.1433382659	-4.3355457697
Н	1.2928783296	-7.0467530961	-4.6745611888
С	3.1298866273	-5.9060898571	-4.7013437059
Н	3.6630603399	-6.6190107315	-5.3319495675
С	3.7428038817	-4.7430150326	-4.2412763104
Н	4.7783802820	-4.5182987990	-4.5048170182
С	3.0191160333	-3.8699799468	-3.4430846695
Н	3.4487113537	-2.9468809467	-3.0561905830
Ν	-2.3015525732	-2.4440933155	-4.6263955407
Н	-1.9428985122	-1.4863263840	-4.4854179595
Н	-3.3177787867	-2.3434807616	-4.6485160942
Н	-2.0312705863	-2.6947101594	-5.5789910396
Ν	2.3508752586	2.4767180426	4.6666581213
H	2.0808161879	2.7273841931	5.6193038532
Н	3.3670884843	2.3759332874	4.6885872405
Н	1.9920383501	1.5190088670	4.5257528897

Table S3. Atoms' cartesian coordinates at equilibrium geometry of the High-Spin (HS) form of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A). Theory/basis set: CAM-B3LYP/pVDZ.

Charge	= 0 Multiplicity	= 5	
Fe	-0.0000731592	0.0003469614	0.0002630938
S	-2.4617339024	1.3377443926	-3.9676468055
Ν	-0.7537553130	0.5068787810	-1.8985055936
Ν	0.4758034250	-2.0628585818	-0.6683163004
Ν	2.1214570380	0.0903359831	-0.5718371630
Ν	3.1163930386	0.9736818841	-0.4530893593
Ν	3.9783945983	-1.0175260695	-0.7765968818
Ν	4.8603888366	-2.0909775970	-0.8588295337
Н	4.9344917194	-2.4724153092	0.1159483004
Н	5.7608675387	-1.6844549032	-1.1232478020
Ν	6.6297494080	0.1727030198	-0.8653884445
С	-1.4628832006	0.8545740282	-2.7664831191
С	-0.4116255144	-3.0422682785	-0.8019515350
Н	-1.4487437351	-2.7879915874	-0.5616535305
С	-0.0460658823	-4.3199005666	-1.2166686206
Н	-0.8026583552	-5.0995343254	-1.3134845150
С	1.2916681053	-4.5684964117	-1.4993049939
Н	1.6143428405	-5.5576600009	-1.8306815539
С	2.2236153188	-3.5454348171	-1.3574476957
Н	3.2839624309	-3.6845176098	-1.5624154206
С	1.7695648923	-2.2957855212	-0.9383377047
С	2.6271150836	-1.1123692009	-0.7759662121
С	4.2458282138	0.3098310497	-0.5691123753
С	5.5809792332	0.9227864568	-0.5190740291
С	7.8416221981	0.7191893665	-0.8364630321
Н	8.6748516087	0.0715629904	-1.1268853569

С	8.0698432014	2.0395492495	-0.4653887093
Н	9.0839000753	2.4418862352	-0.4585275772
С	6.9750467206	2.8229958032	-0.1076322493
Н	7.1101634281	3.8648507274	0.1901500825
С	5.7074821217	2.2614156658	-0.1322270260
Н	4.8154479520	2.8257602732	0.1367061224
S	2.4615485306	-1.3371350500	3.9681852854
Ν	0.7536165497	-0.5062077930	1.8990412985
Ν	-0.4759262596	2.0635556051	0.6688461388
Ν	-2.1215953021	-0.0896195115	0.5724099333
Ν	-3.1165441964	-0.9729504579	0.4536777589
Ν	-3.9785354729	1.0182591994	0.7772401441
Ν	-4.8605360954	2.0917102956	0.8595272284
Н	-4.9347913248	2.4732009282	-0.1152108061
Н	-5.7609826527	1.6851800644	1.1240377832
Ν	-6.6298817415	-0.1719752508	0.8662023472
С	1.4627685128	-0.8539315940	2.7669808216
С	0.4115157492	3.0429553636	0.8024719712
Н	1.4486297614	2.7886641889	0.5621713280
С	0.0459749214	4.3205930447	1.2171880552
Н	0.8025780109	5.1002173976	1.3139976105
С	-1.2917535888	4.5692075472	1.4998318796
Н	-1.6144124932	5.5583761504	1.8312088081
С	-2.2237153306	3.5461585845	1.3579833994
Η	-3.2840589666	3.6852571011	1.5629583696
С	-1.7696848464	2.2965019149	0.9388757345
С	-2.6272513375	1.1130949116	0.7765306072
С	-4.2459755020	-0.3091051535	0.5698012358
С	-5.5811271165	-0.9220669715	0.5198575568
С	-7.8417551761	-0.7184638171	0.8373496616
Η	-8.6749709417	-0.0708316967	1.1277982544
С	-8.0699918522	-2.0388349281	0.4663256672
Η	-9.0840481843	-2.4411743434	0.4595273105
С	-6.9752122655	-2.8222888654	0.1085348034
Н	-7.1103422620	-3.8641521069	-0.1892124917
С	-5.7076476127	-2.2607059667	0.1330493646
Н	-4.8156257906	-2.8250552370	-0.1359149996
Ν	-4.7863956387	2.9274364114	-1.9173102932
Н	-4.0918900987	2.3810783945	-2.4509783790
Н	-4.5121585437	3.9030356242	-2.0441037778
Η	-5.6655032729	2.8204182824	-2.4260324318
Ν	4.7857221010	-2.9264864142	1.9180388495
Η	5.6646452206	-2.8191391103	2.4270026854
Н	4.5117649600	-3.9021665231	2.0448363957
Н	4.0908685835	-2.3803293062	2.4514534325

The calculated Raman spectra of the LS and HS forms of the polymorph **A** of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] are rather similar; nevertheless, intensity or even frequency alterations for some of the peaks are observed (Fig. S9).





Fig. S9. Calculated unscaled (a) low- and (b) high-frequency Raman spectra of the LS and HS forms of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>] (polymorph A) [Raman activity in  $Å^4$ ·(amu)<sup>-1</sup>]. Calculations have been performed at the optimized geometries at the CAM-B3LYP/pVDZ level of theory.

The two most characteristic spectral alterations are noticed in the  $v(C\equiv N)$  peak of the isothiocyanato group which appears ~35 cm<sup>-1</sup> shifted to lower wavenumbers in the spectrum of the HS form [2242 cm<sup>-1</sup> in the HS form (Video S10) and 2276 cm<sup>-1</sup> in the LS form (Video S7)], and in the strong v(C==N)/v(C-C) peak which is at 1596 cm<sup>-1</sup> (Video S9) in the spectrum of the HS form and at 1609 cm<sup>-1</sup> (Video S6) in the LS form spectrum. In the diagnostic low-frequency spectral region, which contains the Fe<sup>II</sup>N<sub>6</sub> vibrations, several modes are recognized. Of particular importance are the peaks which are experimentally observed at 165 and 464 cm<sup>-1</sup>, and whose intensity increases with decreasing temperature. These two peaks are attributed to vibrational modes of the LS state and more precisely to the out-of-plane bending NFeN vibration involving the axial Fe<sup>II</sup>-N<sub>isothiocyanato</sub> bonds (at 166 cm-1) and to the in-plane stretching vibration of the FeN<sub>6</sub> octahedron (at 470 cm<sup>-1</sup>) as extracted from the DFT calculations (Videos S3 and S4). The corresponding HS vibrational modes are calculated at 117 and 456 cm<sup>-1</sup> (Videos S1 and S2), but they are probably of particular low intensity to be observed. The calculated wavenumbers mentioned above have not been scaled by a factor that is usually applied in order to match the experimental values.

**Reduced Raman Representation.** When attempting quantitative/semi-quantitative evaluation of chemical species population through temperature dependent Raman spectra, the use of the known *Reduced Representation Method* is generally required.<sup>10</sup> This representation handles the temperature effect on Raman bands' intensities which critically affects the low frequency spectral region. Typically, the intensity ratio between two distinct Raman bands that correspond to two different species is proportional to their population, with the proportionality constant depending on the Raman cross-section of each vibrational peak as described in the main ms. of the Communication. Nevertheless, in Raman experiments that span a wide range of temperatures, the introduction of such representation is decisive especially if the evaluation of the chemical species population involves both low- and high-frequency bands. The reduction procedure takes into account the fact that the relative intensities of the vibrational lines in a Raman spectrum depend— among other factors—on the population of the vibrational energy levels involved in the scattering process.

Since phonons obey the Boson-type statistics, their mean number at a particular temperature, T, and relative wavenumber, v, is given by:

$$n(\nu, \mathrm{T}) = \left[\exp\left(\hbar\nu/k_B T\right) - 1\right]^{-1}$$
(2)

where  $\hbar$  and  $k_B$  are the Planck and Boltzmann constants, respectively. The stokes-side reduced Raman intensity,  $I^{red}$ , is related to the experimentally measured,  $I^{exp}$ , through the following equation:

$$I^{red}(\nu) = (\nu_o - \nu)^{-4} \nu [n(\nu, T) + 1]^{-1} I^{exp}(\nu)$$
(3)

Equation (3) indicates that if the population ratio is to be extracted through the corresponding peak intensity ratio, the reduced representation is a crucial factor that has to be taken into account in order to cast out the thermal factor in the measured peak intensities. Even though this is a general remark, the reduced representation of the Raman intensities may be tacitly ignored for the specific case of intensity ratios involving peaks positioned in roughly the same frequency.<sup>[11]</sup> On the other hand, if the intensity ratio involves peaks separated by several wavenumbers (especially if one of them is in the low-wavenumber region that is mostly affected), the reduced representation factor should be essentially introduced in the related calculations.

The application of the above mentioned method to our system is illustrated in Fig. S10 below. If the peaks selected for the HS<sup>R</sup> calculation are in close spectral proximity, the effect of reduction procedure is minimal (Fig. S10a) and may be neglected. On the other

hand the effect of reduction on the calculated HS population is critical if the wavenumber difference of peaks selected for its calculation is significant (Fig. S10b).



Fig. S10. Effect of the *Reduced Raman Procedure* on the calculated HS<sup>R</sup> values for two pairs of vibrational peaks, associated with the HS and LS species of the polymorph **A** of *trans*-[Fe(NCS)<sub>2</sub>(abpt)<sub>2</sub>]. (a) The peaks are of comparable energy (2128 cm<sup>-1</sup> and 2090 cm<sup>-1</sup>); (b) the peaks have a significant energy difference (165 cm<sup>-1</sup> and 2090 cm<sup>-1</sup>).

## References

- 1. A.D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 2. P.J. Stephens, C.F. Devlin, M.J. Chabalowski, M.J. Frisch, J. Phys. Chem., 1994, 98, 11623-11627.
- 3. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B, 1988, 37, 785-789.
- 4. T. Yanai, D. Tew, N. Handy, Chem. Phys. Lett., 2004, 393, 51-57.
- Gaussian 09, Revision A.01. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 6. A. Schäfer, H. Horn, R.J. Ahlrichs, *Chem. Phys.*, 1992, **97**, 2571-2577.
- 7. H.E. Mason, W. Li, M.A. Carpenter, M.L. Hamilton, J.A.K. Howard H.A. Sparkes, New J. Chem., 2016, 40, 2466-2478.
- 8. Deposition code: 1422236
- 9. Deposition code: 1422242.
- 10. G.N. Papatheodorou, S.N. Yannopoulos, in *Molten Salts: From Fundamentals to Applications;* Gaume-Escard, M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 2002, pp. 47-106.
- 11. Z.G. Lada, K.S. Andrikopoulos, A. Chrissanthopoulos, S.P. Perlepes, G.A. Voyiatzis, Inorg. Chem., 2019, 58, 5183-5195.