

# Direct observation of light induced spin transitions in new 3,5-bis(2-pyridyl)pyrazolato bridged thiocyanato diiron(II) complexes by monitoring variable temperature laser Raman spectra†

Naohiko Suemura, Mitsuo Ohama and Sumio Kaizaki\*

Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan. E-mail: kaizaki@chem.sci.osaka-u.ac.jp

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The light induced excited spin state trapping LIESST and the reverse LIESST-like phenomena are observed below and above the spin transition temperature, respectively, for new dinuclear diiron(II) complexes and familiar Fe(II) complexes with thiocyanate ligands by monitoring the Raman spectra where only excitation light of various wavelengths for the spectroscopy was used without extra excitation light sources.

There have been a number of investigations concerning spin-crossover phenomena accompanying the spin state transition between the high-spin quintet and the low-spin singlet states of iron(II) complexes.<sup>1</sup> Among them, much attention has recently been paid to light induced excited spin state trapping (LIESST)<sup>2</sup> in relation with molecular switching or information storage from a viewpoint of molecular devices.<sup>3</sup> The thermal spin-crossover and LIESST by temperature variation and irradiation into the d-d or charge transfer transition regions are mainly observed by monitoring magnetic susceptibilities, optical spectra and Mössbauer spectroscopy.<sup>2</sup> On the other hand, there have been several studies of the spin-crossover on the basis of temperature variable vibrational spectroscopy. The Fe-N(NCS) or -N(phen) stretching bands for far IR<sup>4</sup> and the NC(NCS) band for IR<sup>5</sup> and FTIR<sup>6</sup> could be monitored to reveal the spin transitions for *cis*-[Fe(NCS)<sub>2</sub>(phen)<sub>2</sub>] or related complexes. By monitoring the imine stretching band for Raman spectra, the Schiff base complexes were found to exhibit spin equilibrium. Meanwhile, the LIESST of *cis*-[Fe(NCS)<sub>2</sub>(phen)<sub>2</sub>] has been detected by variable temperature FTIR measurement for the NC(NCS) stretching bands.<sup>6</sup> This occurs by irradiation of a low power 632.8 nm He-Ne laser for the calibration of the FTIR spectrophotometer. However, this method utilizes a limited radiation source with a low power and only one wavelength. Much advance in this field is expected to be made by overcoming this disadvantage of limited excitation sources. One of the candidates for easy access to LIESST could be laser Raman spectroscopy with excitation radiation of various wavelengths and variable powers for the spectroscopy itself, but without using any extra light source. Raman spectroscopy has been applied only to differentiating between high- and low-spin Fe(II) complexes<sup>7,8</sup> or estimating the entropy contributions.<sup>8</sup>

This paper reports a successful attempt to observe light induced spin transitions by measuring Raman spectra as a convenient and easily accessible probe. The complexes concerned are new dinuclear diiron(II) complexes bridged by two 3,5-bis(2-pyridyl)pyrazolates (bpyyz) ligands with thiocyanate and pyridine derivatives in the Fe(II) unit, *trans*-(NCS, py-x)-[Fe<sub>2</sub>(NCS)<sub>2</sub>(μ-bpyyz)<sub>2</sub>(py-x)<sub>2</sub>] [py complex (1) and 3-Br-py complex (2)]‡ together with *cis*-[Fe(NCS)<sub>2</sub>(phen)<sub>2</sub>] 3§ and *cis*-

[Fe(NCS)<sub>2</sub>(picen)] (picen = bis(2-pyridylmethyl)ethylenediamine) 4.§ For complexes 1–4, one or two Raman bands are observed around 2070 and 2100 cm<sup>-1</sup> due to the C–N stretching of the NCS<sup>-</sup> ligand. The lower and higher frequency bands correspond to the high- and low-spin complexes 1–4, respectively, and their intensities vary with temperature [Fig. 1 (Figs. S1 and S2†)].¶ The high-spin fractions are approximated as  $n_{HS} = I_{HS}/(I_{HS} + I_{LS})$  where  $I_{HS}$  of the high-spin species around 2070 cm<sup>-1</sup> and  $I_{LS}$  of the low-spin one around 2100 cm<sup>-1</sup> are Raman integrated band intensities at the observed temperatures. Plots of the high-spin fraction from the Raman band intensities vs.  $T$  do not always behave in a similar manner to those obtained from the magnetic susceptibility ( $\chi_M T$ ) as seen in Figs. 2 and 3 (Fig. S3†). At temperatures just below  $T_c$  for complexes 1–3, almost only the low-spin complexes exist as is evident from the  $\chi_M T$  values; ca. 140–80 K for 1, ca. 120–100

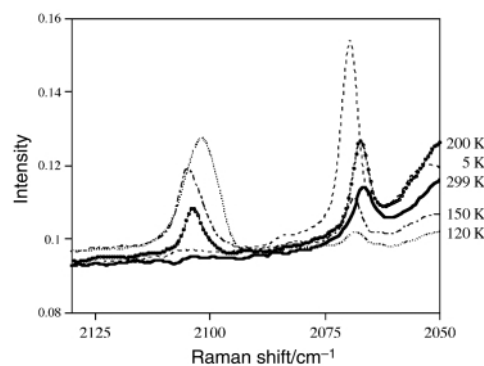


Fig. 1 Variable temperature Raman spectra of complex 1 with excitation of 514.5 nm radiation. (—) 299 K; (---) 200 K; (· · · · ·) 150 K; (- · - · -) 120 K; (- - - - -) 5 K.

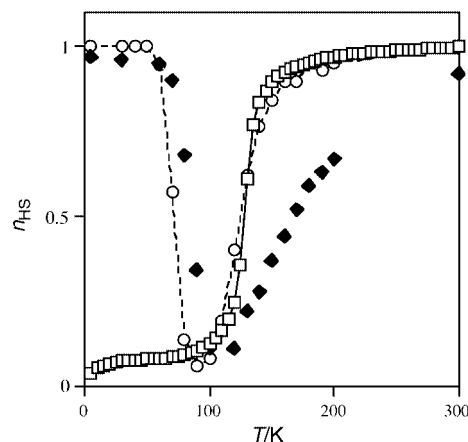
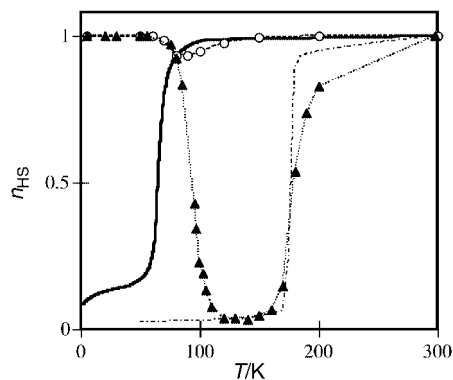


Fig. 2 Plots of the mole fraction of the high-spin state ( $n_{HS}$ ) of complex 1 obtained from the magnetic susceptibility (—□—) and from Raman integrated intensities vs.  $T$ : (---○---) with 632.8 nm radiation, (◆) 514.5 nm radiation.

† Electronic supplementary information (ESI) available: Fig. S1: variable temperature Raman spectra of complex 2 (Ar laser). Fig. S2: variable temperature Raman spectra of complexes 3 and 4. Fig. S3: plots of  $n_{HS}$  of complex 2 from magnetic susceptibility and Raman measurements. Fig. S4: plots of  $n_{HS}$  of complex 3 from magnetic susceptibility and Raman measurements. See <http://www.rsc.org/suppdata/cc/b1/b104121p/>



**Fig. 3** Plots of the mole fraction of the high-spin state ( $n_{\text{HS}}$ ) obtained from magnetic susceptibility measurements: **3** (-----) and **4** (—) and from Raman intensities vs.  $T$ : **3** (---▲---) and **4** (---○---). The magnetic susceptibility and Raman measurements for complex **4** were conducted at a cooling rate of  $0.06 \text{ K min}^{-1}$ .

K for **2** and ca. 170–120 K for **3**. On further cooling, the low-spin fraction decreases and the high-spin state increases as shown in Figs. 2 and 3 (Fig. S3<sup>†</sup>). This observation of the spin transition from low- to high-spin demonstrates the LIESST. The LIESST occurs at the higher temperature with use of shorter wavelength irradiation light (Fig. 2 and Fig. S4<sup>†</sup>). In contrast to a deep drop to 100% of the low-spin fraction between the transition temperatures for **1–3**, complex **4** exhibits a shallow dip below  $T_c$  as shown in Fig. 3. This shallow dip might result from a slow relaxation from high- to low-spin<sup>9b</sup> or could be related to the anomalous spin-crossover phenomenon with hysteresis depending on cooling and heating rates.<sup>9a</sup> This observation suggests that the Raman spectra provide information on the spin-crossover dynamics. For the LIESST of complex **4**, the high-spin fraction was found to be ca. 40% by Mössbauer spectroscopy using broad-band (350–650 nm) excitation with a Xe arc lamp at 10 K,<sup>9b</sup> whereas the high-spin population is 100% according to Raman spectroscopy with a 632.8 nm He–Ne laser around 60 K.

It is noted that the low-spin complexes **1–4** exist even at temperatures above  $T_c$ . This phenomenon is more clearly recognized for the complexes **1** and **2** on measuring the Raman spectra with 514.5 nm Ar laser excitation (Fig. 1 and Fig. S2<sup>†</sup>). The low spin fraction for **1** is ca. 30% around 200 K (Fig. 2), and that for **2** is 15 and 50% at 300 and 118 K, respectively, (Fig. S3<sup>†</sup>). In contrast, almost 100% of the high-spin fraction is found to remain unchanged from the FT-IR<sup>6</sup> of **3** as well as the Raman measurements of **1** and **2** with 632.8 nm He–Ne laser irradiation at this temperature range. This light induced spin transition appears to be a kind of reverse LIESST.<sup>10</sup> However, the experimental conditions of temperature and radiation wavelength are definitely different from each other; the reverse LIESST occurs below  $T_c$  with 820 nm irradiation,<sup>10</sup> whereas the present phenomenon (reverse LIESST-like) is observed above  $T_c$  with 514.5 nm irradiation. This anomalous phenomenon is not clearly elucidated so far. Since both the Raman spectra and LIESST occur for a finite number of molecules<sup>7</sup> or a single molecule,<sup>6c,11</sup> the present Raman measurement may not be

associated with light induced thermal hysteresis (LITH)<sup>11</sup> where the cooperative character affects the relaxation rate.<sup>11b</sup> To our knowledge, this is the first observation of LIESST and reverse LIESST-like phenomena in such a way that the high- and low-spin complexes are spontaneously trapped, respectively, below and above  $T_c$  by irradiation with a Raman spectral excitation laser. These discoveries by Raman spectroscopy will confer advantages to reveal new aspects of the light induced spin transitions by only one radiation source without an extra one.

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## Notes and references

- ‡ These complexes were newly prepared from *trans*-[Fe(NCS)<sub>2</sub>(py)<sub>4</sub>] and Hbpyyz with py-x and characterized to be *trans*-(NCS,py-x)-[(NCS)-(py-x)Fe(μ-bpyyz)<sub>2</sub>Fe(NCS)(py-x)] [ $x = \text{H}$  (**1**) and Br (**2**)] belonging to  $C_{2h}$  [*anti*(NCS)] or  $C_{2v}$  [*syn*(NCS)] point group by the elemental analysis of **1** and **2**, <sup>1</sup>H NMR, and magnetic susceptibility measurement of the analogous complex, *trans*-(NCS,dmsO)-[(NCS)(dmsO)Fe(μ-bpyyz)<sub>2</sub>Fe(NCS)(dmsO)].
- § Complexes **3** and **4** were prepared by the methods detailed in ref. 4(d) and 9(a), respectively.
- ¶ These assignments are made according to ref. 5. Raman spectra were recorded for powdered samples using a Raman excitation He–Ne, Ar or Dye CW unfocused laser beam ( $\phi = 1 \text{ mm}$ ; ca. 3 mW) with 32 scans accumulating at 20 s intervals by a Jasco NR-1800 Raman spectrophotometer. Variable-temperature Raman measurements were performed using an Oxford CF1204 cryostat.
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