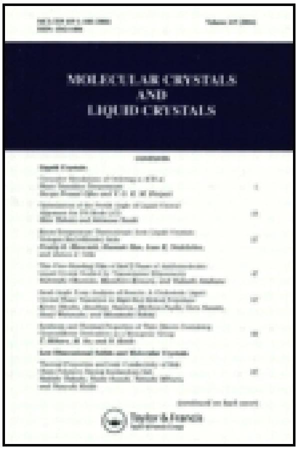


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Anisotropic Effect after Stretching of the Spin-Crossover Compound [Fe(II)(2,6-bis-(benzimidazol-2′-yl)pyridine)$_2$] (C1O$_4$)$_2$ in Polyvinylalcohol Polymer Matrix

Franz Renz [a], Miki Hasegaw [b], Toshihiku Hoshi [b], Usama El-ayaan [c], Wolfgang Linert [c] & Yutaka Fukuda [d]

[a] Institute of Inorganic and Analytical Chemistry, Johannes-Gutenberg University, Staudinger Weg 9, 55022, Mainz

[b] Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Chitosedai 6-16-1, Setagama-ku, Tokyo, 157, Japan

[c] Institute of Inorganic Chemistry, 153, TU-Vienna, Getreide-markt 9, A-1060, Vienna, Austria

[d] Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo, 112, Japan

Version of record first published: 24 Sep 2006

To cite this article: Franz Renz, Miki Hasegaw, Toshihiku Hoshi, Usama El-ayaan, Wolfgang Linert & Yutaka Fukuda (1999): Anisotropic Effect after Stretching of the Spin-Crossover Compound [Fe(II)(2,6-bis-(benzimidazol-2′-yl)pyridine)$_2$] (C1O$_4$)$_2$ in Polyvinylalcohol Polymer Matrix, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 531-540

To link to this article: http://dx.doi.org/10.1080/10587259908028894

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 531-540
Reprints available directly from the publisher
Photocopying permitted by license only

Anisotropic Effect after Stretching of the Spin-Crossover Compound $[Fe(II)(2,6\text{-bis-(benzimidazol-2'-yl)pyridine})_2](ClO_4)_2$ in Polyvinylalcohol Polymer Matrix

FRANZ RENZ[a]*, MIKI HASEGAWA[b], TOSHIHIKU HOSHI[b],
USAMA EL-AYAAN[c], WOLFGANG LINERT[c] and
YUTAKA FUKUDA[d]

[a]*Institute of Inorganic and Analytical Chemistry, Johannes-Gutenberg University, Staudinger Weg 9, 55022 Mainz,* [b]*Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Chitosedai 6–16–1, Setagama-ku, Tokyo 157, Japan,* [c]*Institute of Inorganic Chemistry 153, TU-Vienna, Getreidemarkt 9, A-1060 Vienna, Austria and* [d]*Department of Chemistry, Faculty of Science, Ochanomizu University, 2–1–1 Otsuka, Bunkyo-ku, Tokyo 112, Japan*

$[Fe(II)(2,6\text{-bis-(benzimidazol-2'-yl)-pyridine})_2](ClO_4)_2$ diffused into a poly(vinyl)alcohol polymer matrix, exhibits an thermally induced spin-crossover. After stretching the matrix, the compound orients itself in the matrix. Polarised UV/VIS spectra measured parallel and perpendicular to the stretching direction allowed to calculate the distortion of the molecule in the matrix by means of semi-empirical PPP SCF-CI calculations.

Keywords: spin crossover; PVA; polarized UV/VIS spectroscopy

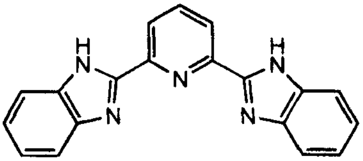
INTRODUCTION

Various iron(II) complexes exhibit a temperature induced spin-crossover between a low-spin (LS) and a high-spin (HS) species.[1] Recently, the iron(II)

---

* *E-mail: renz@ak-guetlich.chemie.uni-mainz.de*

complex [Fe(bzimpy)$_2$](ClO$_4$)$_2$, with the ligand bzimpy = 2,6-bis-(benzimidazol-2′-yl)-pyridine (see SCHEME 1), has been shown to exhibit a pronounced spin-crossover ($^1A_{1g}(O_h) \leftrightarrow {}^5T_{2g}(O_h)$) behavior in both solution[2] and solid state.[3-4] This red-violet solid exhibits solvatochromism when diluted in different solvents.[2] In the present work the [Fe(bzimpy)$_2$](ClO$_4$)$_2$ has been studied in an unstretched and stretched polymer film by means of UV/VIS spectroscopy.



SCHEME 1 bzimpy = 2,6-bis-(benzimidazol-2′-yl)-pyridine

EXPERIMENTAL

The ligand bzimpy (see Scheme 1) as well as the complex [Fe(bzimpy)$_2$](ClO$_4$)$_2$ (**1**) were prepared as described in previous papers.[2] The poly(vinyl)alcohol (PVA) polymer film was prepared as described previously, just PVA in MeOH was used and the stretching was performed at 50°C.[5] The solution and polarized absorption spectra were recorded with a Shimadzu UV-360 type spectrophotometer equipped with a cryostat and a Rochon-type polarizer.[6]

RESULTS

A series of spectra has been measured of **1** in a non-expanding clear-glass-solvent mixture of Ethanol/Methanol (1:1) from 300K down to 15K and in PVA matrix (see FIGURE 1). Clearly the spin-transition was found to exist in both. Polarised UV/VIS investigations exhibited an isotropic behaviour, i.e. no indication for orientation or specific interaction between compound **1** and the matrix. On the other hand the absorption maxima shifted from 556nm to 570nm, indicating a change in the solvation shell. Hence, **1** in PVA polymer matrix behaves like in solution, i.e. "quasi-solution".

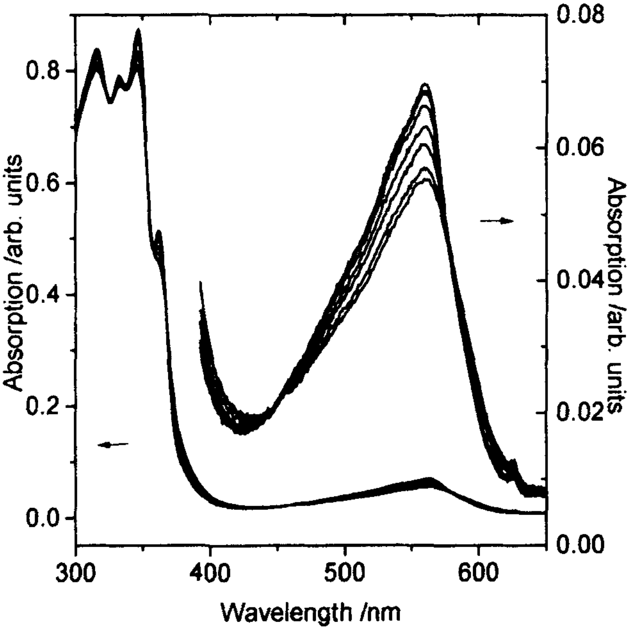


FIGURE 1 UV/VIS spectra of **1** in PVA (Temperatures [K] from bottom: 300, 265, 225, 195, 150, 100, 50, 15)

In the past the spin-crossover in solution was monitored by the ML/LM CT (metal to/from ligand charge transfer) band at 556 nm in MeOH.[2] The peak maximum in PVA is shifted to 570 nm. In the present measurements, additional CT bands located at 362.4, 346.8, 332.5, and 316.2 nm were found to be sensitive for the spin transition (see FIGURE 2).

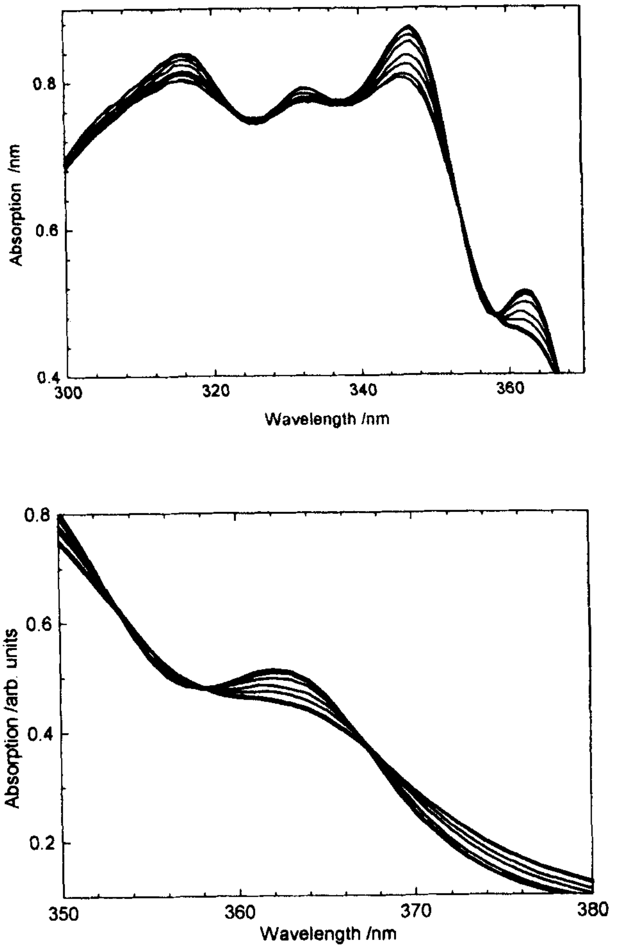


FIGURE 2 Spin-Crossover indicated by several absorptions can be seen in the detail of the UV/VIS spectra of **1** in PVA. All peaks are more intense in the LS (Temperatures [K] at 350 and 360 from bottom: 300, 265, 225, 195, 150, 100, 50, 15).

On cooling they increased in intensity, i.e. because of the bigger extinction coefficient in the low-spin species due to back-donation, i.e. orbital overlap between the metal orbital as donor and the

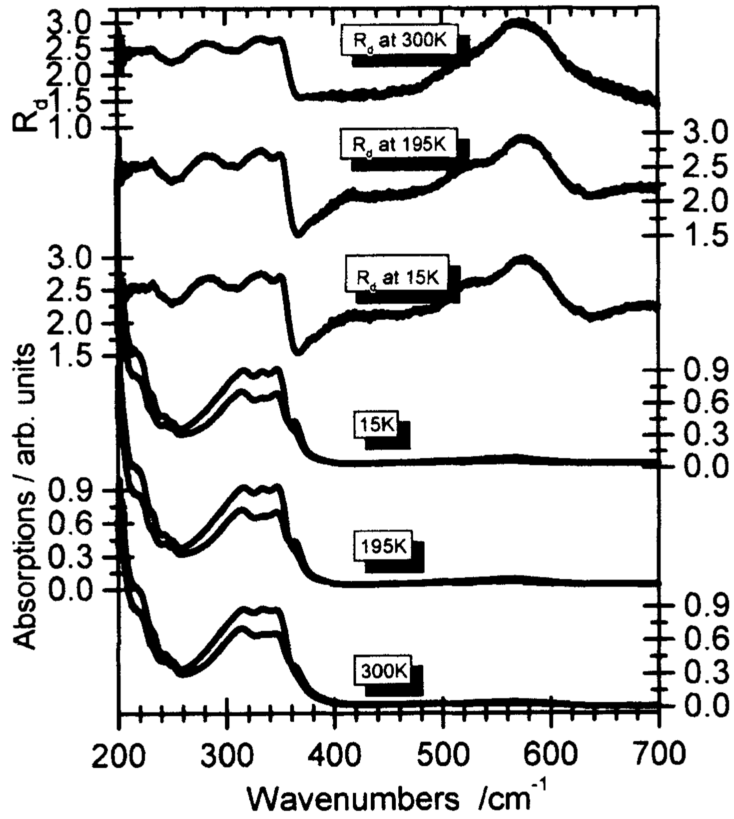


FIGURE 3 Polarised UV/VIS spectra parallel (at 300nm above) and perpendicular (at 300nm below) to the stretching direction at 15K, 195K, 300K. R_d values are given above for each temperature (see EQUATION 1).

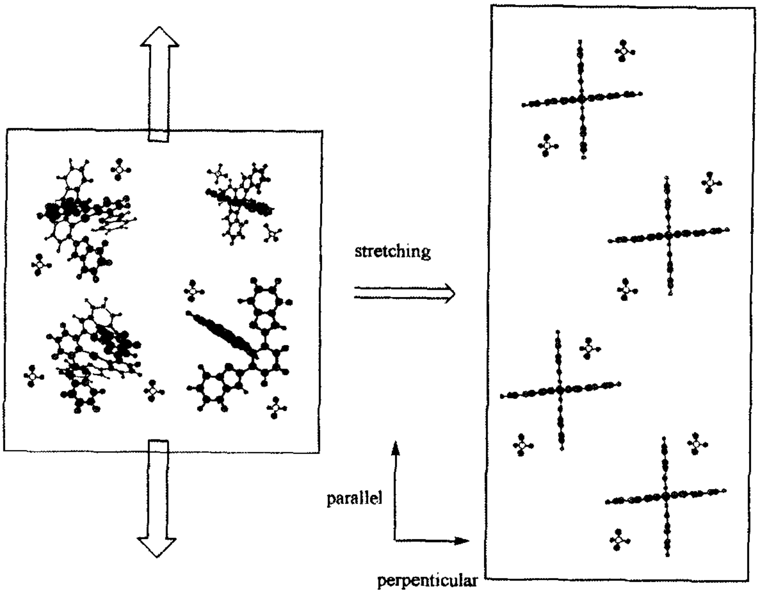
anti-bonding ligand orbitals as acceptor. Out of this five the ones at 362.4 and 570nm were used to describe the spin-crossover. Both bands exhibit a strong maximum in the low-spin state.

In the high-spin state the band at 370nm almost completely disappears. In accordance to previous magnetic measurements, where the spin transition in the solid state revealed pure LS at 100K, we assumed that at 15K (in solution and PVA matrix) only the low-spin species exists.[3] This was supported by IR measurements in CsI and PE matrices, where at 100K the low-spin $\nu_{Fe\text{-}N}$ band was saturated and the high-spin $\nu_{Fe\text{-}N}$ not observable anymore, i.e. pure low-spin.[7] On the other hand, the pure high spin state has not been observed at room temperature.

The UV/VIS spectra of the stretched Polymer were measured at 300K, 195K, and 15K (see FIGURE 3). In this figure, $D_{\parallel}$ and $D_{\perp}$ are optical densities measured with light beams polarized parallel and perpendicular to the stretched direction of the PVA film, respectively. R_d is the ratio of the optical densities $D_{\parallel}$ and $D_{\perp}$ given in the equation

$$R_d = D_{\parallel}/D_{\perp} \qquad (1).$$

A difference between $D_{\parallel}$ and $D_{\perp}$ has been observed, seen in the maxima and minima of R_d. That means, the cationic $[Fe(bzimpy)_2]^{2+}$ has been oriented in the matrix during the stretching, despite its almost spherical shape (see SCHEME 2). Comparison of the stretched spectra at the three temperatures with the unstretched ones exhibits that both directions, $D_{\parallel}$ and $D_{\perp}$, indicate the spin-crossover. At 300K, the band at 362.4 and 570nm shows a strong $D_{\perp}$ and a weak $D_{\parallel}$. On cooling down to 195K both bands in both directions grow due to the increased population of the low-spin state and remain almost constant till 15K (see FIGURE 3).



SCHEME 2 Isotropic arrangement before (left) and oriented arrangement (right) after stretching of compound **1** in the PVA polymer matrix.
See Color Plate VI at the back of this issue.

CALCULATIONS

The orientation of the molecule **1** has been determined by comparison of the electronic spectra with its calculated ones. An PPP approximation (a semi-empirical LCAO-ASMO-SCF-CI), modified for the interpretation of electronic spectra of metal complexes, has been used as described earlier.[8]

Two possible structures for the $[Fe(bzimpy)_2]^{2+}$ have been considered: the x-ray structure[3] with a torsion angle between the two bzimpy-ligand planes of

88 degrees (F88) and another one with 90 degrees (F90) assuming that in solution after dissociation the higher symmetry has been achieved.

TABLE 1 Comparison of the observed and calculated results for **1**

	Transition Energy /nm			Intensity			Polarization		
	Calc. F90	Calc. F88	Obs.[a]	Calc. F90(f)[b]	Calc. F88(f)[b]	Obs.[c] (ε)	Calc. F90	Calc. F88	Obs.[a]
$\pi\pi_1$	341.9	341.7	362.4	1.340	0.957	61.12	Z	Z	s
$\pi\pi_2$	341.4	340.8	346.8	0.725	1.039	108.75	X	X	l
$\pi\pi_3$	328.1	324.0		0.618	0.007		X	Z	
$\pi\pi_4$	322.1	321.2		0.029	0.016		X	Z	
$\pi\pi_5$	318.3	317.6	332.5	0.254	0.372	98.75	Z	X	l
$\pi\pi_6$	316.3	316.7	316.2	0.082	0.366	104.5	Z	Z	s
$\pi\pi_7$	311.7	309.5		0.358	0.013		Z	X	
$\pi\pi_8$	305.9	299.3	305[d]	0.039	2.222	95.00	X	Z	s
$\pi\pi_9$	301.7	298.5		1.345	0.156		X	Z	

[a] observed in the stretched PVA matrix at 15K (s... short axis , l... long axis of the molecule), [b] Oscillator strength, [c] Molar absorptivity observed in the unstretched PVA film at 15K /$10^3dm^3mol^{-1}cm^{-1}$,
[d] shoulder.

In TABLE 1 the results of two calculations are given. While F90 fails, the F88 is able to describe transitions, intensity, and polarization, so that, one bzimpy ligand is rotated into the stretching direction ($D_{\parallel}$), while the second ligand is 2 degrees off from the compressed direction ($D_{\perp}$) (see FIGURE 3, see SCHEME 2). The pure low-spin state exists in the un-stretched PVA film between 15 and 100K, while in the stretched matrix the pure low-spin still exists at 195K. That means that the spin-crossover has been shifted to higher T_c values, i.e. higher transition temperatures. On the other hand the 300K spectra suggest pure high-spin. Hence, the spin crossover became steeper, i.e. shrinked from a temperature interval of more than 300K to less then 100K.

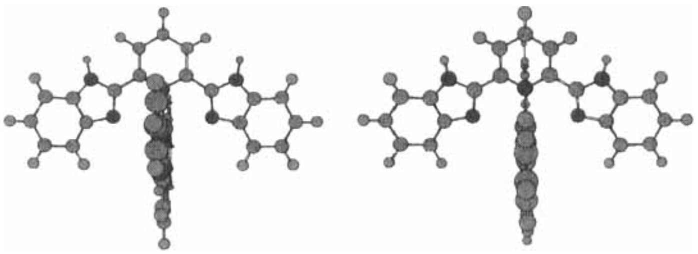


FIGURE 4 Two calculated models F88 and F90 with a LL-torsion angle of 88 and 90 degree. See Color Plate VII at the back of this issue.

This might be originated in the internal anisotropic pressure gradient created during the deformation, while stretching the matrix. To proof this, another experiment has been performed at a smaller stretching rate and the tendency confirmed our assumption. Due to the low concentration of the complex ($8x10^{-5}$ mol/l) a cooperativity among the magnetic centers was not expected.

CONCLUSION

The spin-crossover compound [Fe(II)(2,6-bis-(benzimidazol-2′-yl)-pyridine$)_2$]$(ClO_4)_2$ incorporated into a poly(vinyl)alcohol polymer matrix, exhibits an thermally induced spin-crossover. Hence, the oxygen donor properties of the solid PVA polymer are too weak to destroy compound **1**, in opposite adding compound **1** to a dissolved PVA the bordeaux-red compound almost instantly disappears. After stretching the matrix, the compound orients itself in the matrix. Polarised UV/VIS spectra measured parallel and perpendicular to the stretching direction allowed to calculate the distortion of the molecule in the matrix by means of semi-empirical PPP SCF-CI calculations.

The spin-crossover-compound incorporated polymer stretching is a new method for tuning the spin-crossover behavior.

ACKNOWLEDGMENTS

We thank the "Japanese Society for the Promotion of Science" (F.R. and W.L.), the "Yamada Science Foundation" (W.L.) for staying in Japan, the "Fonds zur Förderung der wissenschaftlichen Forschung in Österreich", project 10818 and 11218, the "Grand in Aids for Scientific Research from the Ministery of Education, Science, Sports and Culture", project 07454173 and 96155, and the EU (TMR-project ERB-FRNX-CT980199) for financial support.

References

[1] P. Gütlich, A. Hauser, and H. Spiering, *Angew. Chem.* **106,** 2109 (1994); P. Gütlich, *Struct. Bonding,* **44,** 83 (1981); E. König, *Struct. Bonding,* **76,** 51 (1991); O. Kahn, *Molecular Magnetism* (VCH, New York, 1993); H. Toftlund, *Coord. Chem. Rev.,* **94,**67 (1989).

[2] A.W. Addison, Sudhir Burman, and C.G.Wahlgren, *J.Chem. Soc. Dalton Trans,* 2621 (1987); W. Linert, M. Konecny, and F. Renz, *J. Chem.Soc. Dalton Trans.,* 1523 (1994).

[3] R. Boca, P. Baran, L. Dlhán, H. Fuess, W. Haase, F. Renz, W. Linert, I. Svoboda, and R. Werner, *Inorg. Chim. Acta,* **260,**129 (1997).

[4] S Rüttimann, C.M. Moreau, A.F. Williams, G. Bernardinelli, and A.W. Addison, *Polyhedron,* **11,** 635 (1992).

[5] T. Hoshi, T. Kawashima, J. Okubo, and M. Yamamoto, *J.Chem. Soc, Perkin Trans.* 1147 (1986).

[6] T. Hoshi, H. Yamamoto, T. Miyauchi, S. Mori, M. Kobayashi, and Y. Tanizaki, *Ber. Bunsenges. Phys. Chem.,* **86,** 330 (1982).

[7] F. Renz, PhD Thesis, Technical University Vienna(AUT), 1997.

[8] M. Hasegawa, Y. Inomaki, T. Inayoshi, T. Hoshi, M. Kobayashi, *Inorg.Chim Acta.,* **257,** 259 (1997).