

Room-temperature spin crossover and Langmuir-Blodgett film formation of an iron(II) triazole complex featuring a long alkyl chain substituent: the tail that wags the dog

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Electronic Supporting Information (ESI)

C₁₆dpt was prepared in three steps according to the general procedure detailed in our earlier paper.¹ The details follow.

***N*-hexadecyl-2-pyridinecarbothioamide**

Hexadecylamine (3.62 g, 15.0 mmol), sulfur (1.44 g, 45.0 mmol) and sodium sulfide nonahydrate (72 mg, 0.30 mmol) were refluxed in 2-picoline (35 mL) for three days, during which time the initially colourless solution turned dark brown. All volatiles were removed under reduced pressure giving a dark brown solid that was taken up in dichloromethane (100 mL) and washed with water (2 x 100 mL). The organic layer was dried over magnesium sulfate and filtered. The resulting clear dark brown solution was filtered through a short pad of silica, and then all solvents were removed under reduced pressure. The resulting red-brown solid was recrystallised from 75 mL boiling ethanol, which yielded an orange-brown powder upon cooling. This was isolated by filtration, washed with ice-cold ethanol (5 mL) and dried thoroughly *in vacuo*. Yield: 3.37 g (62%). ¹H NMR (300 MHz, CDCl₃): δ 8.71 (ddd, $J_{3,4} = 8$ Hz, $J_{3,5} = 1$ Hz, $J_{3,6} = 1$ Hz, 2H, 2 x pyH₃), 8.49 (ddd, $J_{5,6} = 5$ Hz, $J_{4,6} = 2$ Hz, $J_{3,6} = 1$ Hz, 2H, 2 x pyH₆), 7.83 (dt, $J_{3,4} = J_{4,5} = 8$ Hz, $J_{4,6} = 2$ Hz, 2H, 2 x pyH₄), 7.42 (ddd, $J_{4,5} = 8$ Hz, $J_{5,6} = 5$ Hz, $J_{3,5} = 1$ Hz, 2H, 2 x pyH₅), 3.85 (q, $J = 6$ Hz, 2H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.80 (qn, $J = 8$ Hz, 2H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.26 (br s, 26 H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 0.88 (t, $J = 7$ Hz, NH-CH₂-CH₂-(CH₂)₁₃-CH₃).

Ethyl-*N*-hexadecylpyridine-2-carboximidothioate

Freshly rinsed sodium (85 mg, 3.7 mmol) was carefully dissolved in dry ethanol (45 mL). *N*-hexadecyl-pyridine-2-carbothioamide (1.27 g, 3.50 mmol) was added and the orange suspension stirred at room temperature under a calcium chloride drying tube for 30 minutes. Bromoethane (0.28 mL, 0.40 g, 3.7 mmol) was added and the mixture heated to 50 °C for 4 hours, during which time a small amount of white solid precipitated. The mixture was cooled to room temperature, filtered to remove this precipitate, and taken to dryness under reduced pressure. The resulting brown solid was taken up in dichloromethane (50 mL), and washed with water (40 mL), saturated aqueous sodium carbonate (40 mL), saturated brine (40 mL) and water (40 mL), dried (magnesium sulfate) and taken to dryness under reduced pressure. Drying thoroughly *in vacuo* yielded 1.13 g (82%) of a crude brown oil. This material was used without further purification. ¹H NMR (CDCl₃): δ 8.64 (ddd, $J_{5,6} = 5$ Hz, $J_{4,6} = 2$ Hz, $J_{3,6} = 1$ Hz, 2H, 2 x pyH₆), 7.76 (dt, $J_{3,4} = J_{4,5} = 8$ Hz, $J_{4,6} = 2$ Hz, 2H, 2 x pyH₄), 7.60 (ddd, $J_{3,4} = 8$ Hz, $J_{3,5} = 1$ Hz, $J_{3,6} = 1$ Hz, 2H, 2 x pyH₃), 7.30 (ddd, $J_{4,5} = 8$ Hz, $J_{5,6} = 5$ Hz, $J_{3,5} = 1$ Hz, 2H, 2 x pyH₅), 3.85 (q, $J = 7$ Hz, 2H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 2.87 (q, $J = 7$ Hz, 2H, SCH₂CH₃), 1.78 (qn, $J = 7$ Hz, 2H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.25 (br s, 26 H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.10 (t, $J = 7$ Hz, 3H, SCH₂CH₃) 0.88 (t, $J = 7$ Hz, NH-CH₂-CH₂-(CH₂)₁₃-CH₃).

4-Hexadecyl-3,5-bis(2-pyridyl)-triazole ($C_{16}dpt$)

Ethyl-*N*-hexadecylpyridine-2-carboximidothioate (1.56 g, 4.00 mmol) and 2-pyridinecarbohydrazide (0.658 g, 4.80 mmol) were heated to reflux in *n*-butanol (35 mL) for three days hours under a calcium chloride drying tube. The resulting clear dark brown solution was taken to dryness under reduced pressure to give an orange-brown solid. This was taken up in cyclohexane (100 mL), washed with distilled water (2 x 100 mL), and the organic layer dried (magnesium sulfate). The resulting orange-brown solid was further purified by column chromatography (silica, 3:1 diethyl ether:ethyl acetate) giving an analytically clean pale brown powder. Yield: 0.632 g (35%). $C_{28}H_{41}N_5$: calc. C 75.12, H 9.23, N 15.64; found C 74.98, H 9.49, N 15.71%. 1H NMR ($CDCl_3$): δ 8.54 (ddd, $J_{5,6} = 5$ Hz, $J_{4,6} = 2$ Hz, $J_{3,6} = 1$ Hz, 2H, 2 x pyH₆), 8.30 (ddd, $J_{3,4} = 8$ Hz, $J_{3,5} = 1$ Hz, $J_{3,6} = 1$ Hz, 2H, 2 x pyH₃), 7.84 (dt, $J_{3,4} = J_{4,5} = 8$ Hz, $J_{4,6} = 2$ Hz, 2H, 2 x pyH₄), 7.34 (ddd, $J_{4,5} = 8$ Hz, $J_{5,6} = 5$ Hz, $J_{3,5} = 1$ Hz, 2H, 2 x pyH₅), 5.14 (t, $J = 8$ Hz, 2H, trz-CH₂-CH₂-(CH₂)₁₃-CH₃), 2.08 (qn, $J = 7$ Hz, 2H, trz-CH₂-CH₂-(CH₂)₁₃-CH₃), 1.24 (br s, 26 H, NH-CH₂-CH₂-(CH₂)₁₃-CH₃), 0.86 (t, $J = 7$ Hz, trz-CH₂-CH₂-(CH₂)₁₃-CH₃). IR (KBr): $\nu / cm^{-1} = 3050$ (w), 2950 (m), 2918 (vs), 2846 (vs), 1589 (m), 1478 (m), 1478 (m), 1452 (m), 1429 (m), 1380 (w), 1281 (w), 1251 (w), 1148 (w), 994 (w), 797 (w), 740 (w), 710 (w), 691 (w), 622 (w), 564 (w). ESI-MS (pos.): $m/z = 448.3422$, calc for $C_{16}dpt \cdot H^+$ = 448.3435.

[Fe($C_{16}dpt$)₂(NCS)₂] $\cdot \frac{2}{3}H_2O$ (1)

To a clear, colourless solution of $C_{16}dpt$ (100 mg, 0.22 mmol) in 10 mL of dry methanol, under nitrogen, was added, via syringe, a yellow solution of [Fe(py)₄(NCS)₂] (55 mg, 0.11 mmol) in 4 mL dry methanol. This resulted in a red solution that on stirring for 10-15 minutes yielded a purple precipitate (80 mg, 66%). Found: C, 64.57; H, 7.86; N, 15.71; S, 5.63. Calcd. for [Fe^{II}(C₂₈H₄₁N₅)₂(NCS)₂] $\cdot \frac{2}{3}H_2O$ (1097.36 gmol⁻¹): C, 64.54; H, 7.78; N, 15.57; S, 5.94%. IR (KBr): 2919, 2851, 2112 (C \equiv N), 2067 (C \equiv N), 1586, 1482, 1449, 1374, 1147, 995, 793, 739, 708, 601 cm⁻¹. IR (Nujol): 2111 (C \equiv N), 2068 (C \equiv N), 1599, 1585, 1309, 1146, 1093, 1042, 995, 792, 737, 720, 706 cm⁻¹. ESI-MS (pos.): $m/z = 1008.556$ [Fe($C_{16}dpt$)₂(NCS)]⁺.

Crystal structure information for $C_{16}dpt$

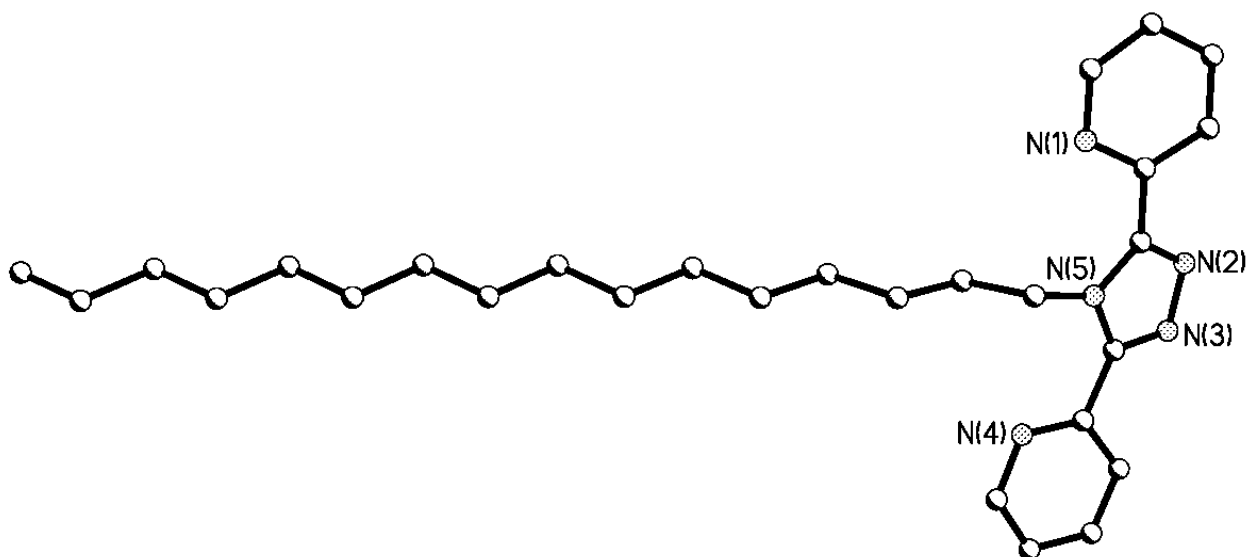


Figure S1: Perspective view of $C_{16}dpt$. Hydrogen atoms omitted for clarity.

Table S1: Crystal data and structure refinement for C₁₆dpt.

	C₁₆dpt
Empirical formula	C ₂₈ H ₄₁ N ₅
<i>M_r</i>	447.66
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> [Å]	65.021(8)
<i>b</i> [Å]	4.6519(4)
<i>c</i> [Å]	17.505(2)
α [°]	90
β [°]	105.188(4)
γ [°]	90
<i>V</i> Å ³	5109.8(10)
<i>Z</i>	8
<i>T</i> [K]	90(2)
$\rho_{\text{calcd.}}$ [g/cm ³]	1.164 Mg/m ³
μ [mm ⁻¹]	0.070 mm ⁻¹
<i>F</i> (000)	1952
Crystal size [mm]	0.50 x 0.21 x 0.19 mm ³
θ range for data collection [°]	0.65 to 26.40°.
Reflections collected	31132
Independent reflections	5212
<i>R</i> (int)	0.0704
Max. and min. transmission	0.9869 and 0.8467
Data / restraints / parameters	5212 / 0 / 300
Goof (<i>F</i> ²)	1.144
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0767
<i>wR</i> ₂ [all data]	0.2012
Max/min res. <i>e</i> density [eÅ ⁻³]	0.545 and -0.446

X-ray data was collected with a Bruker APEX II area detector diffractometer at the University of Otago using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects and semi-empirical absorption corrections (SCALE) were applied. The structure was solved by direct methods (SHELXS-97) and refined against all *F*² data (SHELXL-97).² Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached. All non-hydrogen atoms were made anisotropic. No solvent or disorder present.

Mössbauer spectra of 1

^{57}Fe Mössbauer spectra were recorded by Dr. Guy N. L. Jameson at the University of Otago. Approximately 20 mg of sample was placed in a nylon sample holder (12.8 mm diameter, 1.6 mm thickness) with Kapton windows. Mössbauer spectra were measured on a Mössbauer spectrometer from SEE Co. (Science Engineering & Education Co., MN) equipped with a closed cycle refrigerator system from Janis Research Co. and SHI (Sumitomo Heavy Industries Ltd.). Data were collected in constant acceleration mode in transmission geometry with an applied field of 47 mT perpendicular to the γ -rays. The zero velocity of the Mössbauer spectra refers to the centroid of the room temperature spectrum of a 25 μm metallic iron foil. Analysis of the spectra was conducted using the WMOSS program (SEE Co., formerly WEB Research Co. Edina, MN).

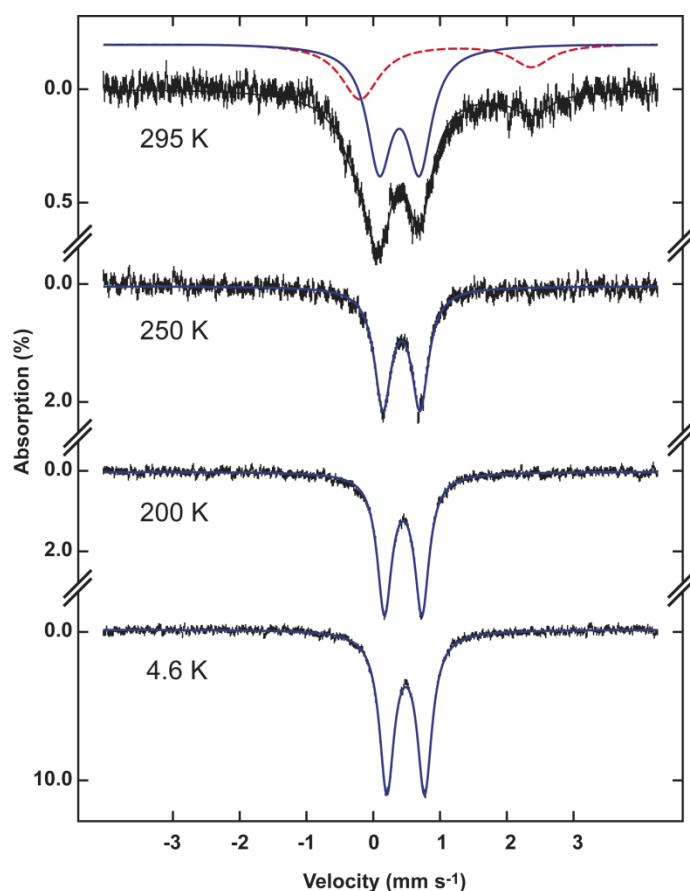


Figure S2. Mössbauer spectra of $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2]$ measured at specified temperatures with an applied field of 47 mT perpendicular to the γ -rays. The significant decrease in the recoilless fraction with increasing temperature is typical of polymeric species with long alkyl chains. The lower temperature spectra (4.6 – 250 K) can each be fitted to a single symmetrical quadrupole doublet with parameters given in Table S2 and Figure S3. The parameters are consistent with LS Fe^{II} . The 295 K spectrum can be fitted using two species: a single quadrupole doublet referring to LS Fe^{II} (blue line) and an asymmetric quadrupole doublet (red dashed line) consistent with HS Fe^{II} . The asymmetry of the HS quadrupole doublet is consistent with either crystal orientation effects or anisotropy of the recoil-free fraction (the Goldanskii-Karyagin effect).

Table S2. The Mössbauer parameters for the LS form of $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2]$ at different temperatures including the isomer shift, the quadrupole splitting, the full width at half maximum and the relative area.

T (K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma_{L=R}$ (mm s^{-1})	I (%)
295	0.38	0.60	0.45	65
250	0.42	0.56	0.31	100
200	0.45	0.56	0.26	100
4.6	0.49	0.57	0.27	100

Table S3. The Mössbauer parameters for the HS form of $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2]$ at 295 K including the isomer shift, the quadrupole splitting the full width at half maximum and the relative area of the absorption at positive and negative velocities (the resonance effect I).

δ (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma_{L=R}$ (mm s^{-1})	I_+ (%)	I_- (%)
1.09	2.47	0.70	10	25

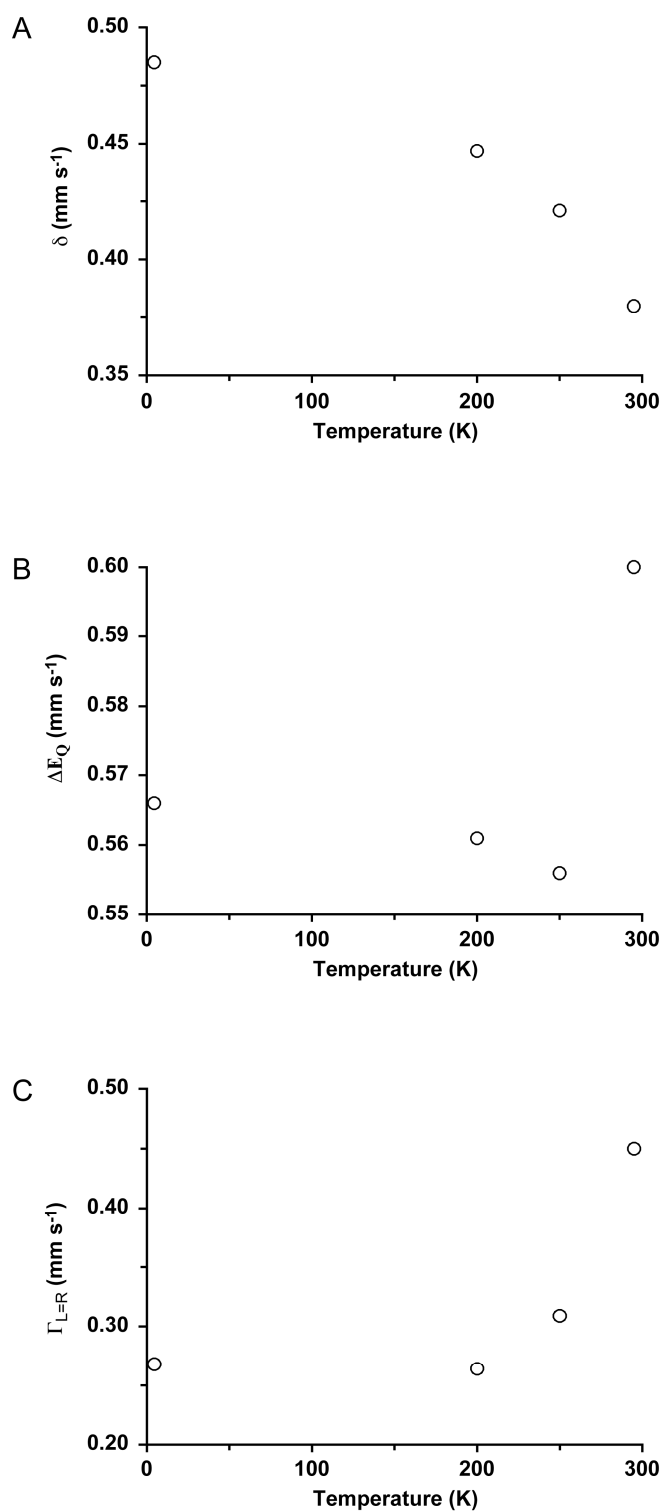


Figure S3. The temperature dependence of the Mössbauer parameters of the HS form of $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2]$. A) Decrease in isomer shift (δ) with increasing temperature. B) Discontinuity in the quadrupole splitting (ΔE_Q) as the compound undergoes spin crossover above 250 K. C) Increase in the line widths (full width at half maximum, Γ) as the compound undergoes spin crossover.

Other

Elemental analysis was carried out by the Campbell Microanalytical Laboratory at the University of Otago.

Infrared spectra were recorded over the range 4000 – 400 cm^{-1} with a Perkin-Elmer Spectrum NBX FT-IR spectrophotometer as a potassium bromide pellet or a Nujol Mull (VT study).

The ESI mass spectrum was recorded on a Bruker MicrOTOF_Q spectrometer, in chloroform/methanol, by Mr Ian Stewart.

Magnetic data were recorded over the range 300 – 4.2 K with a Quantum Design MPMS5 SQUID magnetometer with an applied field of 1 Tesla at Industrial Research Limited (IRL).

Pressure-area isotherms and time stability were measured at 25 °C on a KSV MiniMicro Langmuir-Blodgett trough (KSV, Finland) with a surface area between 1700 and 8700 mm^2 . Water was purified with a Barnstead Nanopure system (Thermo Scientific), and its resistivity was measured to be higher than 18 $\text{M}\Omega \text{ cm}$. Chloroform (puriss. p.a. $\geq 99.8\%$, Fluka) was used as spreading solvent for $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2]$; a 97:3 mixture of chloroform/MeOH for C_{16}dpt . Typically drops (20 μl) of the surfactant solution (0.5 mM) were deposited using a microsyringe on the water subphase. After letting the solvent evaporate for 30 min, the barriers were compressed at 6 mm min^{-1} (3 $\text{cm}^2 \text{ min}^{-1}$) and the surface pressure was monitored using a platinum Willhelmy plate.

References

1. M. H. Klingele and S. Brooker, *Eur. J. Org. Chem.*, 2004, 3422-3434.
2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **A64**, 112-122.