

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

Jonathan A. Kitchen,^a Claudio Gandolfi,^b Martin Albrecht,^{b,c} Guy N. L. Jameson,^a Jeffery L. Tallon^d and Sally Brooker^{*a}

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

$[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2] \cdot \frac{1}{2}\text{H}_2\text{O}$ displays temperature-mediated spin crossover (SCO) with $T_{1/2} = 290$ K and the long alkyl chain substituent on the dipyridyltriazole ligand facilitates the formation of a stable Langmuir-Blodgett film at an air water interface.

The inclusion of 1,2,4-triazole moieties into the coordination sphere of iron(II) can result in the observation of spin crossover (SCO) behaviour.^{1, 2} This switching between the high spin (HS) and low spin (LS) states (bistability) gives rise to possible applications in nano-technology. The viability of such complexes to act as nano-components requires (a) some quite specific properties to be attained (typically SCO at room temperature with a wide hysteresis loop), and (b) the challenges inherent in moving from a molecule to a component ready for use in a device to be overcome.³

Iron(II) complexes of N^4 -substituted-3,5-di(2-pyridyl)-4H-1,2,4-triazoles (**Rdpt**, Fig. 1), in particular the mononuclear complexes $[\text{Fe}^{\text{II}}(\text{Rdpt})_2(\text{NCS})_2]$, have been documented to exhibit SCO. The handful of such complexes in the literature, in which **Rdpt** is **adpt** (red polymorph A, $T_{1/2} = 180$ K,⁴ orange polymorph B, HS;⁵ polymorph C, partial SCO at 86 K,⁶ polymorph D, partial SCO at 162 K⁶), **ptdpt** ($T_{1/2} = 231$ K⁷), **mdpt** (HS⁷) or **pldpt** ($T_{1/2} = 180$ K⁸), have been shown to be mostly SCO active. These studies have also demonstrated that the exact nature of the SCO event is dependent on (a) the choice of N^4 -substituent, (b) the isomer (*cis* or *trans*; to date *cis* forms have been SCO inactive, instead remaining HS^{7, 9}), and (c) the polymorph studied.

This rich vein of SCO active $[\text{Fe}^{\text{II}}(\text{Rdpt})_2(\text{NCS})_2]$ complexes prompted us to widen the range of **Rdpt** ligands employed in such complexes. Here we report the result of extending this to include a new **Rdpt** ligand, N^4 -hexadecyl-3,5-di(2-pyridyl)-4H-1,2,4-triazole (**C₁₆dpt**). Specifically, we detail herein the synthesis and properties of the complex $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2]$. The long alkyl chain N^4 -substituent was chosen as it is known that such chains can facilitate the formation of SCO active Langmuir-Blodgett films on surfaces,¹⁰⁻¹⁵ an attractive feature that allows us to take our first tentative steps towards the long term goal of inclusion of SCO complexes into functional devices.

C₁₆dpt was made according to our general procedure.^{16, 17} Colourless blocks were grown by the slow evaporation of a chloroform solution of **C₁₆dpt** and the X-ray structure was

determined at 89 K (Fig. 2). The ligand crystallises in the monoclinic spacegroup $C2/c$ with one complete molecule in the asymmetric unit (Fig S1). The **dpt** component of this structure is relatively flat, with pyridyl-triazole mean plane angles of $10.1(2)^\circ$ and $18.0(2)^\circ$. The N^4 -hexadecyl chain adopts a *trans* co-planar configuration which is ideal for Langmuir-Blodgett film formation, as it indicates that, at least in the solid state, the preferred arrangement is maximal extension of the chains. These chains interdigitate giving a bi-layer-like appearance (Fig 2).

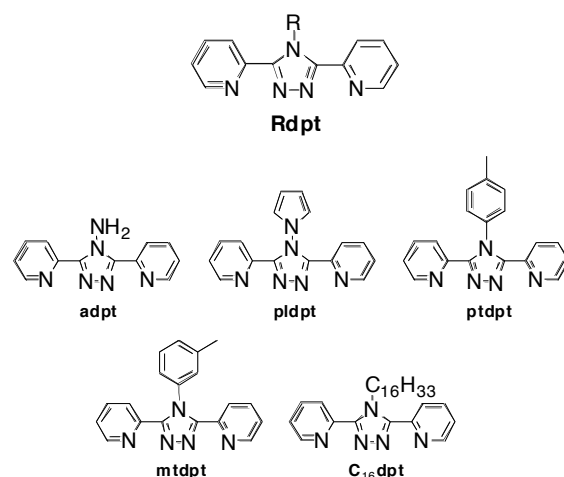


Fig. 1 **Rdpt** ligands utilised in $[\text{Fe}^{\text{II}}(\text{Rdpt})_2(\text{NCS})_2]$ complexes to date (**adpt**, **pldpt**, **ptdpt** and **mdpt**) and the new ligand, **C₁₆dpt**.

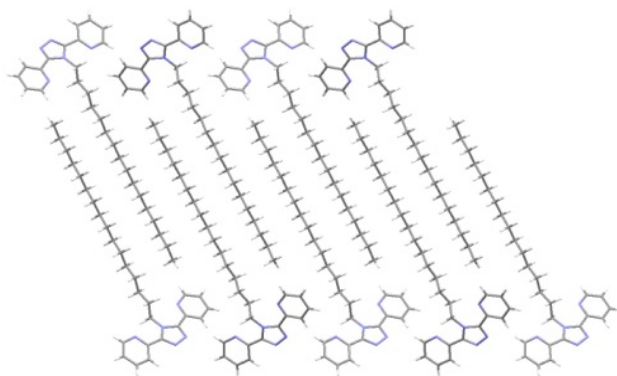


Fig. 2 Perspective view of the packing and layer formation in the crystal structure of **C₁₆dpt**.

When the 2:1 reaction of **C₁₆dpt** with $[\text{Fe}(\text{py})_4(\text{NCS})_2]^{18}$ is carried out under nitrogen in methanol, initially a red solution is obtained. A deep purple precipitate forms in the reaction solution over ten minutes and is isolated by filtration (66% yield). Microanalysis data on the purple solid are consistent with the formula $[\text{Fe}^{\text{II}}(\text{C}_{16}\text{dpt})_2(\text{NCS})_2] \cdot \frac{2}{3}\text{H}_2\text{O}$ (**1**) and the mass spectrum has a peak corresponding to $[\text{Fe}(\text{C}_{16}\text{dpt})_2(\text{NCS})]^{+}$ ($m/z = 1008.5563$ cf calculated value of 1008.5821). The deep purple colour of this complex is indicative of the presence of at least some LS iron(II), and is quite different from the red and orange colours reported for other iron(II) complexes of **Rdpt**.^{4, 5, 7-9, 19}

The temperature dependence of the magnetic susceptibility of **1** was examined from 360 – 4 K (Fig. 3). At 360 K the effective magnetic moment is 5.14 BM, consistent with the presence of fully HS iron(II). On cooling the magnetic moment gradually decreases to 1.28 BM at 200 K, and below 200 K it drops very slowly to 0.71 BM, consistent with the presence of LS iron(II) at low temperatures. This SCO event has a $T_{1/2}$ of 290 K.

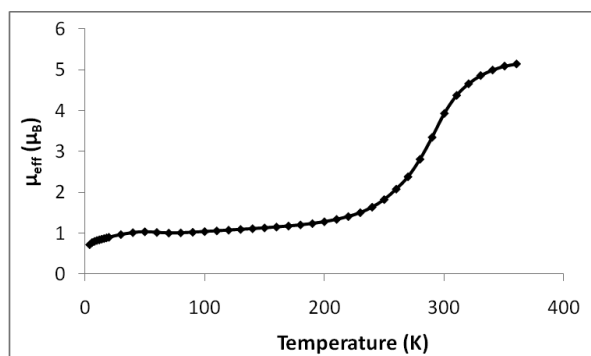


Fig. 3 Plot of μ_{eff} (μ_{B}) vs temperature for **1**. Diamonds are data points; the solid line simply joins data points.

The ^{57}Fe Mössbauer spectra at temperatures < 200 K show a single symmetrical quadrupole doublet (Fig. 4B) with parameters consistent with LS Fe^{II} (Table S2) and a decrease in isomer shift with increasing temperature caused by the second-order Doppler shift.²⁰ At temperatures above 200 K the line width, Γ , of this quadrupole doublet is seen to rapidly increase while the quadrupole splitting also increases with the onset of the spin transition. At 295 K the presence of a second broader asymmetric quadrupole doublet ($\delta = 1.09 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 2.47 \text{ mm s}^{-1}$, $\Gamma_{\text{L}=\text{R}} = 0.70 \text{ mm s}^{-1}$) is clearly observed (Fig. 4A). The asymmetry of this doublet can be explained either through a) orientation effects or b) the anisotropy of the recoil-free fraction (Goldanskii-Karyagin effect²⁰). Orientation effects are likely due to the lipophilic qualities of the C_{16} side-chain of the ligand, but this does not explain the symmetry of the LS form of the complex. However, if the area of the low velocity line is used to quantitate the HS form then a ratio of approximately 40:60 HS:LS is found. This is in reasonable agreement with the magnetic moment at 295 K (NB. the HS \leftrightarrow LS SCO event has $T_{1/2} = 290$ K).

Infrared spectroscopy is a powerful technique for characterising $[\text{Fe}^{\text{II}}(\text{Rdpt})_2(\text{NCS})_2]$ complexes⁷ as the $\text{C}\equiv\text{N}$ stretching frequency of the thiocyanate group is sensitive to the spin state of the iron(II) to which it is bound. At room

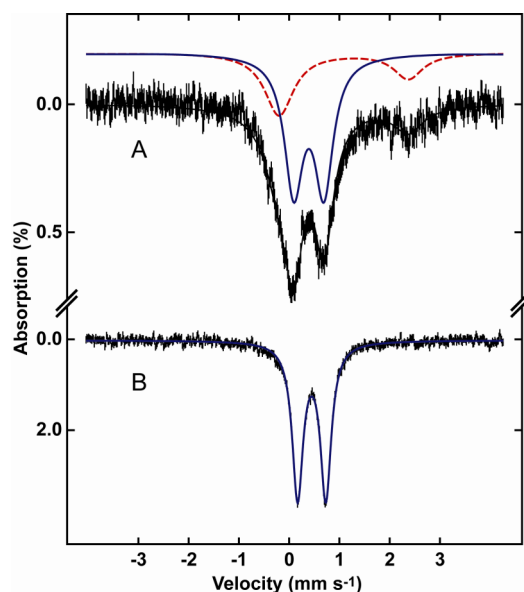


Fig. 4 Mössbauer spectra of **1** measured at A) 295 K and B) 200 K. Spectrum B is fitted (blue line) to a single symmetrical quadrupole doublet with parameters consistent with LS Fe^{II} ($\delta = 0.45 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 0.56 \text{ mm s}^{-1}$, $\Gamma_{\text{L}=\text{R}} = 0.26 \text{ mm s}^{-1}$). Spectrum A can be fitted with two quadrupole doublets: a symmetrical one (blue line, $\delta = 0.38 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 0.60 \text{ mm s}^{-1}$, $\Gamma_{\text{L}=\text{R}} = 0.45 \text{ mm s}^{-1}$) and an asymmetric one (red dashed, $\delta = 1.09 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 2.47 \text{ mm s}^{-1}$, $\Gamma_{\text{L}=\text{R}} = 0.70 \text{ mm s}^{-1}$) consistent with a mixed HS:LS state approximately 40:60.

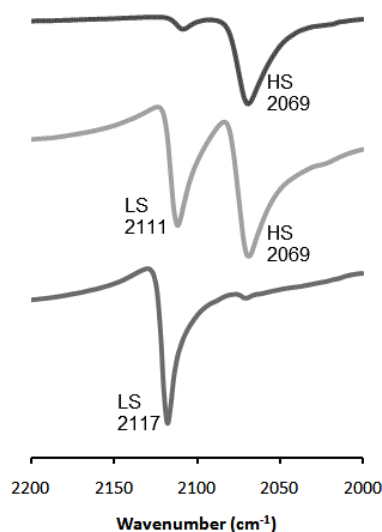


Fig. 5 Observed thiocyanate stretching frequencies for **1** as a Nujol mull after heating with a hot air gun (top, HS), at room temperature (middle, HS and LS) and after immersion in liquid nitrogen (bottom, LS).

temperature a Nujol mull of **1** showed two $\text{C}\equiv\text{N}$ stretches [2069 and 2111 cm^{-1} , Fig. 5]. When the sample was cooled by immersion in liquid nitrogen and the spectrum quickly obtained, only one strong peak, at 2117 cm^{-1} , was observed, consistent with the presence of the LS species. Conversely, when the sample was heated up with a hot air gun, again only one strong peak was observed, but at 2069 cm^{-1} which is indicative of the presence of the HS species. These findings are consistent with the magnetic and Mössbauer data.

The self-assembling properties of this amphiphilic complex, **1**, were investigated at the air-water interface. Formation of Langmuir films was indicated by the pertinent pressure-area isotherms (Fig. 6). Gradual transition from liquid-expanded phases to liquid-condensed and solid phases is reflected by the exponential increase of the surface pressure.²¹ Film collapse occurred at approximately 37 mN m⁻¹, corresponding to a minimum area of ca. 60 Å² per molecule. This value compares well with the molecular dimension of unfunctionalized [Fe(dpt)₂(NCS)₂], 63 Å², as extracted from crystallographic data. It is slightly higher than the calculated area for two alkyl chains, viz. 44 Å² per molecule,^{22,23} and hence suggests a supramolecular organization of the complexes which comprises the polar Fe₂(dpt)₂ fragments oriented towards the water phase and the hydrophobic C₁₆H₃₃ tails pointing out in a less dense arrangement. Notably, the free ligand C₁₆dpt also formed stable Langmuir films, with a similar collapsing pressure, providing a molecular area that is in good agreement with other alkyl-based amphiphiles. Both films, comprised of the ligand as well as those comprised of complex **1**, revealed excellent stability properties (inset Fig. 6). No pressure decrease was noted upon keeping a film at the liquid-condensed state for a prolonged period of time (> 3h). It is interesting to note that a complementary approach, in which we utilised amphiphilic anions in our complexes, [Fe(Rdpt)₂(C₁₆SO₃)₂] where Rdpt is either adpt or pldpt, did not afford stable films, despite the crystal structure determination on the adpt complex confirming that in the solid state the anions are coordinated to the iron centre.²⁴ Clearly the covalent attachment of the apolar moiety to the Rdpt ligand (i.e. synthesis of C₁₆dpt) entails significant additional synthetic effort over the use of the amphiphilic anion, but it appears to substantially improve the self-assembling ability of the resulting Rdpt complexes.

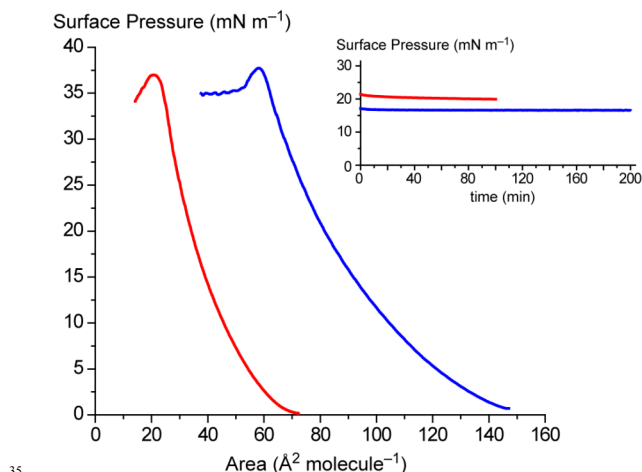


Fig. 6 Pressure-area isotherms; inset shows pressure-time profiles for Langmuir films of [Fe^{II}(C₁₆dpt)₂(NCS)₂] (blue) and C₁₆dpt (red).

In conclusion, the present study showcases the complex [Fe(C₁₆dpt)₂(NCS)₂] which has the highest T_{1/2} (290 K) yet observed for a [Fe^{II}(Rdpt)₂(NCS)₂] complex. This T_{1/2} is in the ideal range for functional devices, i.e. systems that operate at or near room temperature. Furthermore, we have observed the formation of a stable Langmuir-Blodgett film at the air-water

interface, a property that is highly desirable as we look to move towards attaching functional molecules to surfaces, with the ultimate goal of making components for use in devices.

This work was supported by grants from the University of Otago, MacDiarmid Institute for Advanced Materials and Nanotechnology, RSNZ Marsden Fund, and Swiss National Science Foundation. We thank Mr N.G. White (Brooker group) for preparing C₁₆dpt.

Notes and references

- ^a Department of Chemistry and MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, PO Box 56, Dunedin 9054 (New Zealand) E-mail: sbrooker@chemistry.otago.ac.nz
- ^b Department of Chemistry, University of Fribourg, Chemin du Musée 9, CH-1700 Fribourg (Switzerland)
- ^c School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, (Ireland)
- ^d MacDiarmid Institute for Advanced Materials and Nanotechnology and Industrial Research Limited, PO Box 31310, Lower Hutt (New Zealand)
- † Electronic Supplementary Information (ESI) available: [synthesis and full Mössbauer data for **1**, crystallographic information and additional view of C₁₆dpt (CCDC 773454), and general information on techniques used]. See DOI: 10.1039/b000000x/
- J. G. Haasnoot, *1,2,4-Triazoles as ligands for iron(II) high spin-low spin crossovers*, Kluwer Academic Publishers, Dordrecht, 1996.
- O. Kahn and E. Codjovi, *Philos. Trans. R. Soc. London, Ser. A.*, 1996, **354**, 359-379.
- S. Brooker and J. A. Kitchen, *Dalton Trans.*, 2009, 7331-7340.
- N. Moliner, M. C. Muñoz, S. Letard, J.-F. Letard, X. Solans, R. Burriel, M. Castro, O. Kahn and J. A. Real, *Inorg. Chim. Acta*, 1999, **291**, 279-288.
- A. B. Gaspar, M. C. Muñoz, N. Moliner, V. Ksenofontov, G. Levchenko, P. Gülich and J. A. Real, *Monatsh. Chem.*, 2003, **134**, 285-294.
- C.-F. Sheu, S.-M. Chen, S.-C. Wang, G.-H. Lee, Y.-H. Liu and Y. Wang, *Chem. Commun.*, 2009, 7512-7514.
- D. Zhu, Y. Xu, Z. Yu, Z. Guo, H. Sang, T. Liu and X. You, *Chem. Mater.*, 2002, **14**, 838-843.
- J. A. Kitchen, G. N. L. Jameson, J. L. Tallon and S. Brooker, *Chem. Commun.*, 2010, DOI: 10.1039/b927036a.
- J. A. Kitchen and S. Brooker, *Coord. Chem. Rev.*, 2008, **252**, 2072-2092.
- J. T. Culp, J.-H. Park, D. Stratakis, M. W. Meisel and D. R. Talham, *J. Am. Chem. Soc.*, 2002, **124**, 10083-10090.
- H. Soyler, C. Mingotaud, M.-L. Boillot and P. Delhaes, *Langmuir*, 1998, **14**, 5890.
- O. Kahn, F. Armand, C. Badoux, P. Bonville and A. Ruadel-Teixier, *Langmuir*, 1995, **11**, 3467-3472.
- P. Coronel, A. Barraud, R. Claude, O. Kahn, A. Ruadel-Teixier and J. Zarembowitch, *J. Chem. Soc., Chem. Commun.*, 1989, 193-194.
- A. Ruadel-Teixier, A. Barrauda, P. Coronel and O. Kahn, *Thin Solid Films*, 1988, **160**, 107-115.
- O. Roubeau, B. Agricole, R. Clérac and S. Ravaine, *J. Phys. Chem. B*, 2004, **108**, 15110-15116.
- M. H. Klingele and S. Brooker, *Eur. J. Org. Chem.*, 2004, 3422-3434.
- J. A. Kitchen, D. S. Larsen and S. Brooker, *Chem. Asian J.*, 2010, **5**, 910-918.
- H. Huang and T. Ogawa, *J. Mol. Struct.*, 2006, 21-26.
- N. Moliner, M. C. Muñoz, P. J. van Koningsbruggen and J. A. Real, *Inorg. Chim. Acta*, 1998, **274**, 1-6.
- N. N. Greenwood and T. C. Gibb, *Mössbauer spectroscopy*, Chapman and Hall Ltd, London, 1971.
- M. C. Petty, *Langmuir-Blodgett Film: An Introduction*, Cambridge University Press, Cambridge, 1996.
- R. Johann and D. Vollhardt, *Mater. Sci. Eng., C*, 1999, **8-9**, 35-42.
- D. K. Chattoraj, E. Halder, K. P. Das and A. Mitra, *Adv. Colloid Interface Sci.*, 2000, **123-126**, 151.
- N. G. White, H. L. C. Feltham, C. Gandolfi, M. Albrecht and S. Brooker, *Dalton Trans.*, 2010, **39**, 3751-3758.

Contents entry

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