



HAL
open science

Thermal and Light-Activated Spin Crossover in Iron(III) qnal Complexes

Warisa Thammasangwan, Phimpaka Harding, Shane G. Telfer, Adil Alkaş, Wasinee Phonsri, Keith S. Murray, Rodolphe Clérac, Mathieu Rouzières, Guillaume Chastanet, David J. Harding

► **To cite this version:**

Warisa Thammasangwan, Phimpaka Harding, Shane G. Telfer, Adil Alkaş, Wasinee Phonsri, et al.. Thermal and Light-Activated Spin Crossover in Iron(III) qnal Complexes. *European Journal of Inorganic Chemistry*, 2020, 2020 (14), pp.1325-1330. 10.1002/ejic.202000115 . hal-02569914

HAL Id: hal-02569914

<https://hal.science/hal-02569914v1>

Submitted on 8 Sep 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Thermal and light-activated spin crossover in iron(III) qnal complexes

Warisa Thammasangwan,^[a] Phimphaka Harding,^[a] Shane G. Telfer,^[b] Adil Alkaş,^[b] Wasinee Phonsri,^[c] Keith S. Murray,^[c] Rodolphe Clérac,^[d] Mathieu Rouzières,^[d] Guillaume Chastanet,^[e] and David J. Harding*^[a]

[a] Functional Materials and Nanotechnology Center of Excellence, Walailak University, Thasala, Nakhon Si Thammarat, 80160, Thailand
E-mail:hdavid@mail.wu.ac.th. www.funtechwu.com

[b] MacDiarmid Institute for Advanced Materials and Nanotechnology, Institute of Fundamental Sciences, Massey University, New Zealand

[c] School of Chemistry, Monash University, Clayton, Melbourne, Victoria, 3800, Australia

[d] CNRS, UMR 5031, Centre de Recherche Paul Pascal (CRPP), 115 avenue du Dr. Albert Schweitzer, Pessac, F-33600, France

[e] CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr A. Schweitzer, Pessac, F-33608, France

Supporting information for this article is given via a link at the end of the document

Abstract: Three iron(III) complexes, $[\text{Fe}(\text{qnal})_2]\text{Y}$ (qnal = 1-[(8-quinolinylimino)methyl]-2-naphthalenolate; Y = NO_3 **1**, $\text{BPh}_4\text{-CH}_2\text{Cl}_2$ **2**, NCS **3**) have been prepared to explore anion effects in spin crossover systems. Structural studies on **2** reveal 1D chains formed by $\pi\text{-}\pi$ and C-H $\cdots\pi$ interactions between the $[\text{Fe}(\text{qnal})_2]^+$ cations. SQUID magnetometry shows the onset of spin crossover in **1** at high temperature, while gradual but complete spin crossover is observed in **2** and **3** with $T_{1/2} = 285$ and 340 K, respectively. Unusually, **2** also undergoes LIESST at 980 nm with ca. 65% efficiency and T(LIESST) = 25 K and reverse-LIESST at 660 nm with full reversibility over many cycles. The results highlight the important influence that the anion has on thermal and light-activated spin crossover properties.

Introduction

Spin crossover (SCO) may be observed in first row transition metal complexes which have a $d^4\text{-}d^7$ electron configuration and an octahedral geometry.^[1-6] In these complexes, there are two possible spin states: high spin (HS, maximum number of unpaired spins) and low spin (LS, minimum number of unpaired spins). Provided that the ligand field is suitable so both spin states can be accessed, they can be switched by changes in external stimuli such as temperature,^[7,8] pressure,^[9] light^[10,11] or application of a magnetic field. The switching may occur over a temperature range of several hundred or just a few Kelvin. The latter is termed abrupt SCO and occurs when the spin centers are strongly linked to each other through cooperative elastic interactions.^[12,13] In cases where this cooperativity is particularly high, the SCO may be accompanied by hysteresis. It follows that design of SCO complexes with strong cooperativity requires the careful use of supramolecular contacts such as hydrogen^[14-19] and halogen bonding,^[20-23] and $\pi\text{-}\pi$ stacking.^[24-34]

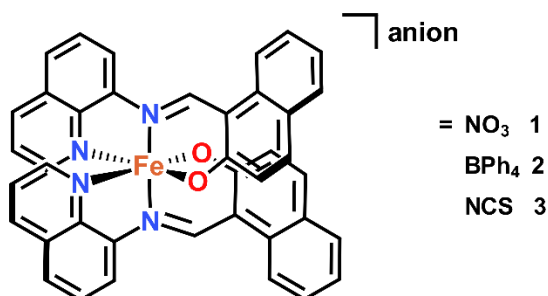
Cooperativity is also important in light activated spin crossover systems. These were first reported in 1984, when Gütllich and co-workers observed a photo-induced LS \rightarrow HS transition in the iron(II) complex, $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$.^[35] They called this process the light-induced excited spin state trapping (LIESST) effect. Subsequent work revealed that LIESST occurs through an excited state that, after intersystem crossing, relaxes to the HS state.^[36] Relaxation back to the original LS state is prevented, at low temperatures, by the large difference in the Fe-N bond lengths, which in the case of Fe(II) is typically around 0.20

Å.^[2] As a consequence in iron(III) systems where the change in bond lengths between the HS and LS state is smaller,^[37,38] ca. 0.13 Å, it was long believed that LIESST could not occur. However, in 2000 Hayami and co-workers reported the first example of LIESST in $[\text{Fe}^{\text{III}}(\text{pap})_2]\text{ClO}_4\cdot\text{H}_2\text{O}$.^[39] The reason for the strong LIESST effect in this compound is the highly distorted HS Fe(III) center which results in a high energy barrier slowing the relaxation process.^[31]

Several years later Takahashi *et al.* reported $[\text{Fe}(\text{qnal})_2][\text{Pd}(\text{dmit})_2]_5\cdot\text{acetone}$ (qnal = 1-[(8-quinolinylimino)methyl]-2-naphthalenolate) which shows gradual SCO, and a weak LIESST effect.^[40] Using the same qnal ligand, the two solvates $[\text{Fe}(\text{qnal})_2]\text{OTf}\cdot\text{acetone}$ and $[\text{Fe}(\text{qnal})_2]\text{OTf}\cdot\text{MeOH}$ were reported with both showing abrupt SCO with a hysteresis of 11 and 3 K, respectively.^[41] Interestingly, despite its smaller hysteresis the acetone solvate shows better LIESST properties being almost 100 % compared with 50% for the MeOH solvate highlighting the fact that there seems to be no direct correlation between thermal hysteresis and LIESST.^[42] $[\text{Fe}(\text{qnal-OMe})_2]\text{PF}_6\cdot\text{acetone}$ and $[\text{Fe}(\text{qnal-OMe})_2]\text{BPh}_4\cdot 2\text{MeOH}$ (qnal-OMe = 7-methoxy-1-[(8-quinolinylimino)methyl]-2-naphthalenolate), also exhibit SCO behavior with thermal hysteresis loops ($T_{1/2}\uparrow = 202$ K, $T_{1/2}\downarrow = 194$ K for acetone and $T_{1/2}\uparrow = 304$ K, $T_{1/2}\downarrow = 194$ K for MeOH).^[43] Moreover, a strong LIESST effect was observed in both compounds. Trapping the SCO complex in a halogenated framework has also been used to improve LIESST characteristics to great effect in $[\text{Fe}(\text{qsal})_2][(\text{C}_6\text{F}_3\text{I}_3)]$ with LIESST almost 100%.^[23] Reverse-LIESST is also present in this compound and $[\text{TMA}][\text{Fe}(\text{azp})_2]$ (TMA = tetramethylammonium; azp = 2,2'-azodiphenolate); the latter having an impressive T(LIESST) of ca. 80 K (T(LIESST) being the relaxation temperature above which the photo-induced state is erased upon warming at 0.4 K·mn).^[10,11,44] Recent work by some of us has shown how light reveals a large hidden hysteresis in $[\text{Fe}(\text{naphBzen})_2]$ (naphBzen = 1-[(2-(benzylamino)ethylimino)methyl]-2-naphtholate).^[45]

The foregoing illustrates that light activation in iron(III) SCO systems remains rare and it seems that the ligand is of primary importance in observing LIESST. Moreover, anion effects in iron(III) SCO systems are still little studied and contrasting results are observed. For instance, in $[\text{Fe}(\text{qsal-5-OMe})_2]\text{Y}$ (qsal-5-OMe = (8-quinolyl)-5-methoxysalicylaldehyde; Y = BF_4 , NCS, PF_6 , BPh_4) $T_{1/2}$ is dependent on the anion size,^[46] while for $[\text{Fe}(\text{Him})_2(\text{hapen})]\text{Y}\cdot\text{sol}$ {hapen = N,N'-bis(2-

hydroxyacetophenylidene)ethylenediamine; Y = BF₄, ClO₄, PF₆, CF₃SO₃, BPh₄; sol = solvent} only intermediate sized anions result in SCO active systems with the other complexes HS.^[47] Therefore, we have undertaken the study of a series of compounds [Fe(qnal)₂]Y (Y = NO₃ **1**, BPh₄·CH₂Cl₂ **2**, NCS **3**; see below) which exploit the qnal ligand. The structural, magnetic and light activation of these compounds is reported herein.



Results and Discussion

Synthesis and IR spectroscopy

The complexes were prepared by layered diffusion from a solution of Hqnal in CH₂Cl₂ with NEt₃ added over which a MeOH solution of the appropriate iron(III) salt was added. The poor solubility of the Hqnal ligand in CH₂Cl₂, once prepared, necessitated making the ligand *in situ*. In all cases the compounds are isolated as black solids.

IR spectroscopy of the Fe(III) complexes shows a broad band around 3408-3450 cm⁻¹ typical of an O-H group due to small amounts of water as a result of high humidity (Table 1, Figure S1). The weak bands around 3040-3057 cm⁻¹ are aromatic C-H stretches. The complexes show a strong intensity C=N stretch for the imine of the qnal ligand at 1613-1614 cm⁻¹.^[41,48] The N-O stretch from the nitrate is found around 1380 cm⁻¹, while the C≡N stretch from the NCS⁻ anion is at 2065 cm⁻¹.

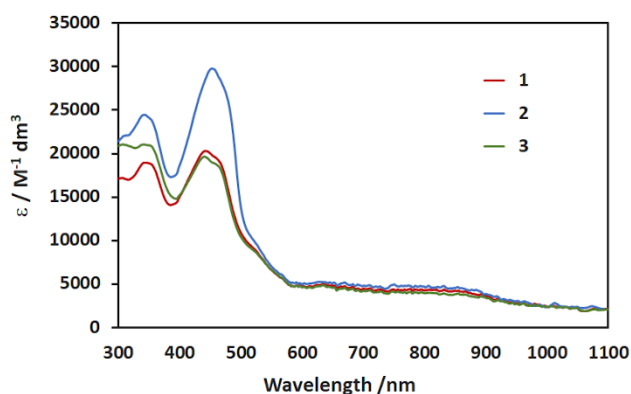


Figure 1. UV-Vis spectra of [Fe(qnal)₂]Y in DMF.

UV-Vis spectroscopy

The UV-Vis spectra of all complexes in DMF reveal two absorption regions, one at 342-345 nm and another region at 442-470 nm with two broad bands. The higher energy band is assigned to a $\pi \rightarrow \pi^*$ transition involving the qnal ligand. The band

at 450 nm, in line with the related [Fe(qsal-X)₂]⁺ complexes,^[26,48,49] is most probably a ligand-to-metal charge transfer band (LMCT). It is notable when comparing these complexes with [Fe(qsal-X)₂]⁺ that the LMCT band is more intense probably due to the naphthalene moiety of the qnal ligand. We also undertook reflectivity measurements on **2** which showed a thermally induced modification of the spectrum between 270 and 10 K ($\Delta R = 0.039$ a.u. at 675 nm), suggesting a stable LS state below 220 K and a conversion to a HS state that is not complete at 270 K as shown in the magnetic data, *vide infra*. Interestingly, the band at 1,000 nm, seen in the solid-state spectra, is absent in solution but this may reflect the poor solubility of **2** in DMF which permitted only a low concentration spectrum to be recorded. This also prevented us from determining the spin state of the compounds in solution using the Evan's method.

Table 1. IR and UV-Vis spectroscopic data of [Fe(qnal)₂]Y complexes.

Complex	IR (cm ⁻¹) ^[a]			λ_{max} /nm (ϵ_{max} /M ⁻¹ cm ⁻¹)
	VC-H	VC=N	Vanion	
1	3049)w(1614)m(1380)s(345)18875(, 442)19560(
2	3057)w(1613)s(-	342)24605(, 453)29785(
3	3040)w(1613)s(2065)m(343)21010(, 445)19815(

[a] Absorptions: s= strong, m = medium, w = weak. Complexes were determined in KBr.

Structural studies on [Fe(qnal)₂]BPh₄·DCM

Repeated attempts were made to crystallize **1** and **3** but we were unable to obtain crystals of sufficient quality for X-ray crystallography. In contrast, [Fe(qnal)₂]BPh₄·DCM crystallized well using the layered diffusion method. Single crystal X-ray diffraction analysis of the structure at 123 and 293 K shows the compound crystallizes in the triclinic space group $P\bar{1}$ with one BPh₄ anion and one CH₂Cl₂ molecule in the asymmetric unit at both temperatures (see Table S1 for data and refinement details).

Table 2. Fe-N/O bond lengths and octahedral distortion parameters (Å, °) for **2**.

	123 K	293 K
Fe-O1	1.878(5)	1.885(6)
Fe-O2	1.885(4)	1.902(5)
Fe-N1	1.980(8)	2.037(8)
Fe-N2	1.988(6)	2.087(7)
Fe-N3	1.962(8)	2.035(8)
Fe-N4	1.987(5)	2.083(6)
$\Delta\text{Fe-O}_{\text{ave}}$		0.012
$\Delta\text{Fe-N}_{\text{ave}}$		0.081
$\Sigma^{\text{[a]}}$	46.7	54.2
$\Theta^{\text{[b]}}$	131.4	190.1

[a] Ref.50. [b] Ref. 51.

As expected, the Fe(III) centre has an N_4O_2 donor set with the two qnal ligands enforcing a *cis*-configuration. The Fe-O and Fe-N bond lengths are 1.882 Å and 1.979 Å, respectively at 123 K and consistent with a LS electronic configuration (Table 2).^[40,41,43,48] As the sample is heated to room temperature these bond distances lengthen by 0.012 and 0.081 Å and suggest that while significant spin crossover has taken place it is incomplete at this temperature. The octahedral distortion parameters^[50–52] mirror this trend further supporting this conclusion.

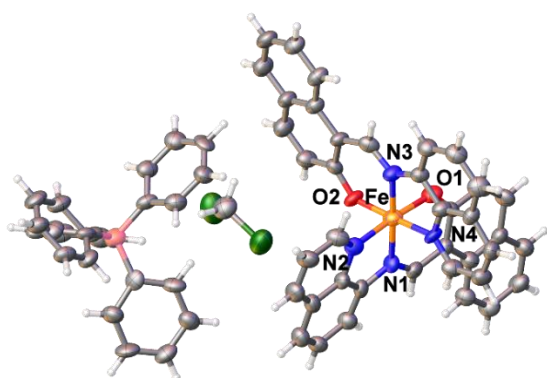


Figure 2. View of the asymmetric unit of **2** at 123 K showing the labelling of the coordination sphere.

In terms of packing, the complex shows a displaced π - π interaction with a centroid-to-centroid distance of 3.79 Å (plane-to-plane distance = 3.33 Å) indicative of a π - π interaction. At 293 K, the centroid-to-centroid distance increases to 3.88 Å while the plane-to-plane distance remains comparatively similar (3.35 Å). The π - π interaction is supported by a pair of C-H...O contacts giving a dimer. The dimers are then connected by a pair of C-H... π interactions, 2.70 Å (2.74 Å at 293 K) forming a 1D chain (Figure 3). The 1D chain is decorated by BPh_4^- anions which interact through multiple C-H... π contacts. The BPh_4^- anions sit between the 1D chains of the $[Fe(qnal)_2]^+$ cations resulting in a 2D sheet with some overlap of the qnal ligands (purple region, Figure 4, Figure S3).

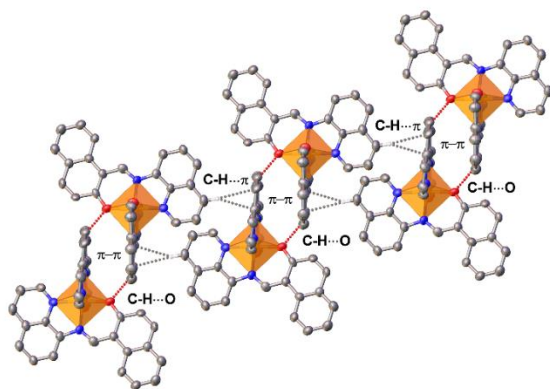


Figure 3. View of the π - π dimers and C-H... π interactions that link the dimers in **2** at 123 K. Solvent molecules and the BPh_4^- anions have been removed in the interests of clarity.

The structure of **2** is similar to the published structure of $[Fe(qnal)_2]CF_3SO_3 \cdot sol$ in which the same 2D sheets form via connection of the π - π dimers by pairs of C-H... π interactions, although the relative position of the 1D chains is slightly different.^[41] $[Fe(qnal)_2][naphthalenyl-SO_3]$ also contains π - π dimers but these are connected by P4AE interactions.^[48] However, the structure of **2** differs from $[Fe(qnal)_2][Pd(dmit)_2]_5 \cdot acetone$ ^[40] and $[Fe(qnal)_2][pyrene-SO_3] \cdot MeOH \cdot CH_2Cl_2$ ^[53] where 1D chains are formed by orthogonal π - π interactions. The reason for this difference is unclear and suggests that $[Fe(qnal)_2]^+$ complexes may have a greater degree of flexibility in their packing than the related $[Fe(qsal-X)_2]^+$ systems.

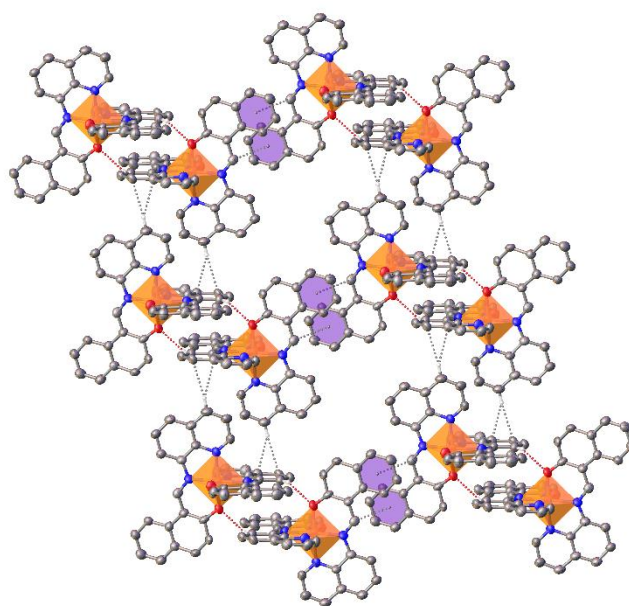


Figure 4. View of the π - π interactions that link the 1D chains of the π - π dimers.

Magnetic studies on $[Fe(qnal)_2]Y$

The magnetic properties of **1-3** were studied by SQUID magnetometry and are presented as $\chi_M T$ versus T plot in Figure 5. The $\chi_M T$ value of **1** is 0.60 $cm^3 K mol^{-1}$ at 200 K and typical of LS Fe(III).^[41,48,54–57] Heating shows a very gradual increase in the value of $\chi_M T$ to approximately 1.50 $cm^3 K mol^{-1}$ at 360 K suggesting ca. 25% HS.

The $\chi_M T$ value of **2** is 0.60 $cm^3 K mol^{-1}$ at 50 K again suggesting full LS Fe(III). Heating the sample results in a gradual increase reaching approximately 4.4 $cm^3 K mol^{-1}$ at 380 K indicating that the sample is fully HS.^[41,48,54–57] This process is reversible and rules out SCO occurring as a result of solvent loss. This is confirmed by TGA measurements where a 6.5% mass loss (8.0% calculated) consistent with CH_2Cl_2 occurs between 170–195 °C (see Figure S4). The reason for the high temperature loss of the solvent likely relates to the structure in which the CH_2Cl_2 molecules are trapped in pockets by the cations and anions. Thus, the spin crossover is gradual with $T_{1/2}$ ca. 285 K. LIESST studies on powdered samples of **2** to investigate the photomagnetic properties were done by illuminating the sample at 980 nm at 5 K for 1 hour (Figure 5b). Near-IR wavelengths have been used to excite other Fe(III)-qnal complexes and research suggests that this is due to a spin-allowed ligand to metal charge transfer

(LMCT) transition.^[41,43,58] The $\chi_M T$ value increases to $2.9 \text{ cm}^3 \text{ K mol}^{-1}$ after irradiation indicating ca. 65% conversion of the LS state to the metastable HS state, one of the most efficient LIESST conversions reported for Fe(III). Upon heating the sample to 30 K, relaxation back to the LS state occurs. The LIESST temperature, determined by the $\partial\chi_M T/\partial T$ derivative, shows that T(LIESST) is 25 K. A slightly higher $\chi_M T$ value of $3.05 \text{ cm}^3 \text{ K mol}^{-1}$ is observed after heating to 390 K but the relaxation curve is identical to that before heating and again suggests little or no desolvation. It is unusual for a complex exhibiting such a high $T_{1/2}$ to undergo LIESST and appears to suggest that the qnal ligand is particularly effective at light-activation (see Table S2).

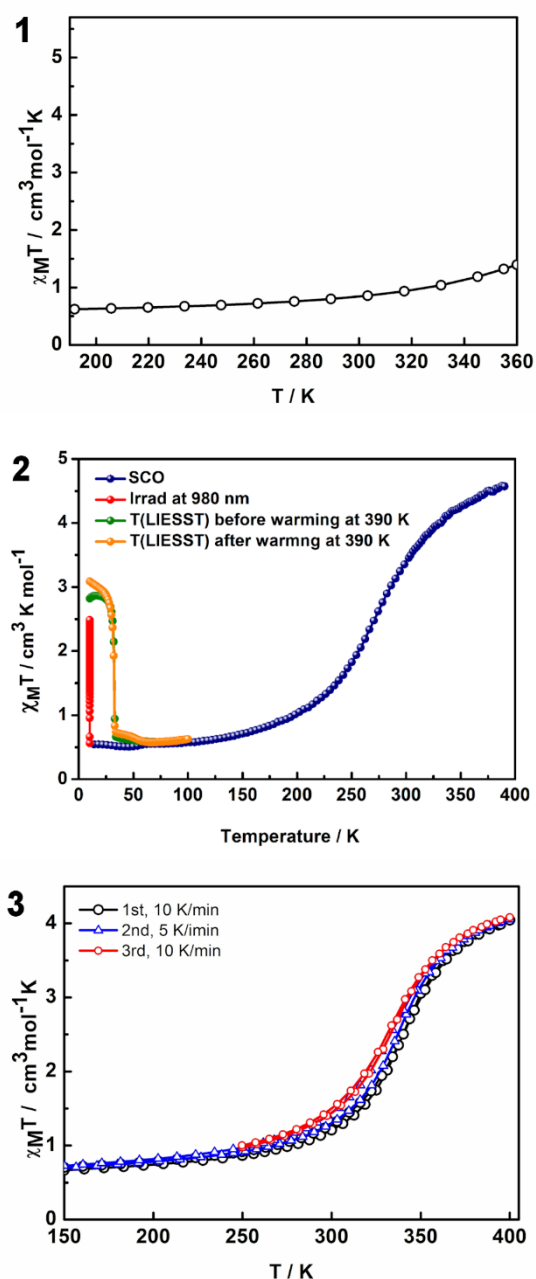


Figure 5. $\chi_M T$ versus T plots for 1-3.

Reflectivity studies on powdered samples confirm that following irradiation at 940 nm at 10 K the spectrum matches that recorded at 270 K indicating conversion to a metastable HS state. Subsequent irradiation at 660 nm results in a return to the LS state showing that **2** also undergoes *reverse*-LIESST. Successive irradiation at 940 nm and 660 nm shows that the photoexcitation is fully reversible over many cycles (Figure S2). To date only [TMA][Fe(azp)₂]^[44] and [Fe(naphBzen)₂]^[45] have been shown to exhibit *reverse*-LIESST. Further studies are currently underway to better understand the photoexcitation in **2**.

Complex **3** shows a very similar SCO profile to **2**. The $\chi_M T$ value is $0.7 \text{ cm}^3 \text{ K mol}^{-1}$ at 150 K and typical of LS Fe(III). Upon heating the $\chi_M T$ value increases at ca. 300 K reaching $4.0 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K and indicative of almost complete SCO, with $T_{1/2}$ ca. 340 K. The higher $T_{1/2}$ compared with **2** and the weaker LIESST typically associated with higher spin transition temperatures meant that the light activation of **3** was not explored.^[59] Interestingly, the SCO profile is also similar to [Fe(qnal)₂][Pd(dmit)₂]₅·acetone^[40] although it is shifted to higher temperature by 120 K and indicates that both the size and the shape of the anion can be used to tune SCO properties.

Conclusion

In summary, we have successfully prepared three new Fe(III) SCO complexes. Structural studies of **2** revealed extensive π - π , C-H... π and C-H...O interactions that link the cations into 2D sheets. While the nitrate complex shows only the onset of SCO, the BPh₄ and NCS compounds exhibit gradual SCO at or above room temperature. Unusually, [Fe(qnal)₂]₂BPh₄·DCM also reveals significant LIESST with T(LIESST) around 25 K and *reverse*-LIESST, with reversible photoswitching between the spin states. These results also suggest that smaller anions tend to favour the LS state in [Fe(qnal)₂]⁺ complexes mirroring the trend observed in the [Fe(qsal-5-OMe)₂]⁺ system. Moreover, it appears that the qnal ligand does indeed seem to favour LIESST and provided that suitable anions can be found, it is likely that further light activated cooperative SCO systems are waiting to be discovered.

Experimental Section

General remarks

All manipulations were performed in air with reagent-grade solvents. All other chemicals were purchased from Sigma-Aldrich or TCI Chemicals and used as received. Infrared spectra were collected as KBr discs on a Bruker Tensor 27 FT-IR spectrometer in the range of 400-4000 cm^{-1} using OPUS software for data collection. Electronic spectra were recorded in DMF (0.1-1.0 mM) at room temperature on an Avantes spectrophotometer in combination with Avalight-DHC and Avaspec ULS2048XL-USB2 in the range 268-1000 nm.

X-ray crystallography

Crystallographic data of [Fe(qnal)₂]₂BPh₄·DCM were collected at 123 and 298 K using a Rigaku Spider diffractometer equipped with MicroMax MM007 rotating anode generator Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$), high-flux Osmic multilayer mirror optics, and a curved image-plate detector.^[60] X-ray diffraction by crystals of [Fe(qnal)₂]₂BPh₄·DCM was inherently weak. Multiple specimens were screened, but none diffracted to high angles. During refinement, the data were truncated at the point where the

diffraction signal dropped into the noise (1.16 Å at 123 K and 1.25 Å at 298 K). Nonetheless, the structure of the complex was unambiguous and refinement proceeded smoothly. CheckCIF alerts A that relate to this weak diffraction and consequently low data:parameter ratio exist. The structures were then solved by direct methods and refined on all F^2 data using SHELX.^[61,62] Hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters which were about 1.2 × (aromatic CH) or 1.5 × (CH₂) the equivalent isotropic thermal parameters of their parent carbon atoms. All pictures were generated with OLEX2.^[63] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1967474-1967475 (293 and 123 K, respectively).

Magnetic Susceptibility Studies

Data were collected with a Quantum Design MPMS 5 SQUID magnetometer under an applied field of 1 T over the temperature range 5–360 K for [Fe(qnal)₂]NO₃ and 5–400 K for [Fe(qnal)₂]BPh₄-DCM and [Fe(qnal)₂]NCS. The powdered or polycrystalline samples were placed in gel capsules and care was taken to allow long thermal equilibration times at each temperature. The photomagnetic properties were recorded using an optical fibre connected on one side to a set of photodiodes and irradiating the sample inside the SQUID cavity on the other side. The irradiation intensity was set to prevent any consequent warming effect.^[10]

Synthesis of [Fe(qnal)₂]NO₃ 1

A solution of Hqnal was prepared in a test tube by first preparing a solution of 8-aminoquinoline (0.0577 g, 0.4 mmol) and 2-hydroxy-1-naphthaldehyde (0.0689 g, 0.4 mmol) in dichloromethane (2 mL). Then, a blank methanol solution (2 mL) was layered in the middle of the test tube as a buffer layer. Finally, a solution of Fe(NO₃)₃·9H₂O (0.0808 g, 0.2 mmol) in methanol (1 mL) was layered on top. The test tube was sealed and left at room temperature. After a week, black microcrystals formed at the bottom and side. The product was washed with diethyl ether (2 mL) and air dried (0.0896 g, 60%). Elemental analysis: calcd (found) for C₄₀H₂₆N₅O₅Fe: C, 67.43 (67.65); H, 3.67 (3.55); N, 9.83 (9.48).

Synthesis of [Fe(qnal)₂]BPh₄-DCM 2

Complex **2** was synthesized via a similar method to **1** but using NaBPh₄ mixed with FeCl₃ to form Fe(BPh₄)₃ instead of Fe(NO₃)₃·9H₂O. After a week, black block crystals had formed at the bottom and side of the test tube. The product was washed with diethyl ether (3 mL) and air dried (0.1207 g, 62%). Elemental analysis: calcd (found) for **2** (C₆₅H₄₈N₄O₂BCl₂Fe): C, 74.17 (74.45); H, 4.60 (4.29); N, 5.32 (5.33).

Synthesis of [Fe(qnal)₂]NCS 3

Complexes **3** was synthesized in a similar method to **1** using KNCS mixed with FeCl₃ to form Fe(NCS)₃ instead of Fe(NO₃)₃·9H₂O. After a week, black microcrystals formed at the bottom and side. The product was washed with diethyl ether (3 mL) and air dried (0.0837g, 60%). Elemental analysis: calcd (found) for **3** (C₄₁H₂₆N₅O₅SFe): C, 63.50 (63.69); H, 3.70 (3.30); N, 9.88 (9.77).

Acknowledgements

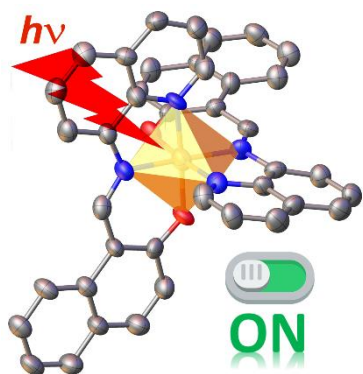
We gratefully acknowledge the Thailand Research Fund (BRG6180008) for funding this research. The Development and Promotion of Science and Technology Talents project is thanked for a scholarship to WT. We also thank the Franco-Thai Mobility Programme for traveling costs (PHC-SIAM 40746YH). KSM acknowledges receipt of an Australian Research Council Discovery grant (DP170102980).

Keywords: spin crossover • iron(III) complexes • light-induced excited spin state trapping • X-ray crystallography

- [1] M. A. Halcrow, Ed. , *Spin-Crossover Materials: Properties and Applications*, John Wiley & Sons, Ltd, Chichester, **2013**.
- [2] P. Güttlich, H. A. Goodwin, *Top. Curr. Chem.* **2004**, 233, 1–47.
- [3] K. S. Murray, in *Spin-Crossover Mater. Prop. Appl.* (Ed.: M.A. Halcrow), John Wiley & Sons Ltd., Chichester, **2013**, pp. 1–54.
- [4] M. Halcrow, *Crystals* **2016**, 6, 58.
- [5] E. Collet, P. Guionneau, *Comptes Rendus Chim.* **2018**, 21, 1133–1151.
- [6] S. Brooker, *Chem. Soc. Rev.* **2015**, 44, 2880–2892.
- [7] J. A. Real, A. B. Gaspar, M. C. Muñoz, *Dalton Trans.* **2005**, 2062–2079.
- [8] J. Linares, E. Codjovi, Y. Garcia, *Sensors* **2012**, 12, 4479–4492.
- [9] V. Ksenofontov, A. B. Gaspar, P. Güttlich, *Top. Curr. Chem.* **2004**, 235, 23–64.
- [10] G. Chastanet, C. Desplanches, C. Baldé, P. Rosa, M. Marchivie, P. Guionneau, *ChemSq* **2018**, 2, 2.
- [11] J.-F. Létard, *J. Mater. Chem.* **2006**, 16, 2550–59.
- [12] M. A. Halcrow, *Chem. Soc. Rev.* **2011**, 40, 4119–42.
- [13] K. S. Murray, C. J. Kepert, *Top. Curr. Chem.* **2004**, 233, 195–228.
- [14] X. H. Zhao, S. L. Zhang, D. Shao, X. Y. Wang, *Inorg. Chem.* **2015**, 54, 7857–7867.
- [15] Z. Ni, A. M. McDaniel, M. P. Shores, *Chem. Sci.* **2010**, 1, 615–621.
- [16] J. S. Costa, S. Rodríguez-Jiménez, G. A. Craig, B. Barth, C. M. Beavers, S. J. Teat, G. Aromí, *J. Am. Chem. Soc.* **2014**, 136, 3869–74.
- [17] M. C. Young, E. Liew, R. J. Hooley, *Chem. Commun.* **2014**, 50, 5043–5045.
- [18] T. Shiga, R. Saiki, L. Akiyama, R. Kumai, D. Natke, F. Renz, J. M. Cameron, G. N. Newton, H. Oshio, *Angew. Chemie - Int. Ed.* **2019**, 58, 5658–5662.
- [19] I. Nemeč, R. Herchel, Z. Trávníček, *Dalton Trans.* **2015**, 44, 4474–4484.
- [20] K. Fukuroi, K. Takahashi, T. Mochida, T. Sakurai, H. Ohta, T. Yamamoto, Y. Einaga, H. Mori, *Angew. Chem. Int. Ed.* **2014**, 53, 1983–6.
- [21] N. Nassirinia, S. Amani, S. J. Teat, O. Roubeau, P. Gamez, *Chem. Commun.* **2014**, 50, 1003–5.
- [22] I.-R. Jeon, O. Jeannin, R. Clérac, M. Rouzières, M. Fourmigué, *Chem. Commun.* **2017**, 53, 4989–4992.
- [23] I.-R. Jeon, C. Mathonière, R. Clérac, M. Rouzières, O. Jeannin, E. Trzop, E. Collet, M. Fourmigué, *Chem. Commun.* **2017**, 53, 10283–10286.
- [24] G. A. Craig, J. S. Costa, O. Roubeau, S. J. Teat, G. Aromí, *Chem. - Eur. J.* **2012**, 18, 11703–11715.
- [25] G. Aromí, C. M. Beavers, J. Sánchez Costa, G. A. Craig, G. Mínguez Espallargas, A. Orera, O. Roubeau, *Chem. Sci.* **2016**, 7, 2907–2915.
- [26] S. E. Lazaro, A. Alkaş, S. J. Lee, S. G. Telfer, K. S. Murray, W. Phonsri, P. Harding, D. J. Harding, *Dalton Trans.* **2019**, 48, 15515–15520.
- [27] R. Pritchard, C. A. Kilner, M. A. Halcrow, *Chem. Commun.* **2007**, 577–9.
- [28] T. D. Roberts, F. Tuna, T. L. Malkin, C. A. Kilner, M. A. Halcrow, *Chem. Sci.* **2012**, 3, 349.
- [29] K. Takahashi, M. Okai, T. Mochida, T. Sakurai, H. Ohta, T. Yamamoto, Y. Einaga, Y. Shiota, K. Yoshizawa, H. Konaka, et al., *Inorg. Chem.* **2018**, 57, 1277–1287.
- [30] S. Hayami, Z.-Z. Gu, H. Yoshiki, A. Fujishima, O. Sato, *J. Am. Chem. Soc.* **2001**, 123, 11644–50.

- [31] S. Hayami, K. Hiki, T. Kawahara, Y. Maeda, D. Urakami, K. Inoue, M. Ohama, S. Kawata, O. Sato, *Chem. Eur. J.* **2009**, *15*, 3497–3508.
- [32] W. Phonsri, D. S. Macedo, K. R. Vignesh, G. Rajaraman, C. G. Davies, G. N. L. Jameson, B. Moubaraki, J. S. Ward, P. E. Kruger, G. Chastanet, et al., *Chem. Eur. J.* **2017**, *23*, 7052–7065.
- [33] D. J. Harding, W. Phonsri, P. Harding, K. S. Murray, B. Moubaraki, G. N. L. Jameson, *Dalton Trans.* **2015**, *44*, 15079–15082.
- [34] N. Phukkaphan, D. L. Cruickshank, K. S. Murray, W. Phonsri, P. Harding, D. J. Harding, *Chem. Commun.* **2017**, *53*, 9801–9804.
- [35] S. Decurtins, P. Gütllich, C. P. Köhler, H. Spiering, A. Hauser, *Chem. Phys. Lett.* **1984**, *105*, 3–6.
- [36] A. Hauser, *J. Chem. Phys.* **1991**, *94*, 2741–48.
- [37] P. J. van Koningsbruggen, Y. Maeda, H. Oshio, *Top. Curr. Chem.* **2004**, *233*, 259–324.
- [38] D. J. Harding, P. Harding, W. Phonsri, *Coord. Chem. Rev.* **2016**, *313*, 38–61.
- [39] S. Hayami, Z. Gu, M. Shiro, Y. Einaga, A. Fujishima, O. Sato, *J. Am. Chem. Soc.* **2000**, *122*, 7126–7127.
- [40] K. Takahashi, H.-B. Cui, Y. Okano, H. Kobayashi, H. Mori, H. Tajima, Y. Einaga, O. Sato, *J. Am. Chem. Soc.* **2008**, *130*, 6688–89.
- [41] T. Shimizu, Y. Komatsu, H. Kamihata, Y. H. Lee, A. Fuyuhiko, S. Iijima, S. Hayami, *J. Incl. Phenom. Macrocycl. Chem.* **2011**, *71*, 363–369.
- [42] N. Paradis, F. Le Gac, P. Guionneau, A. Largeteau, D. Yufit, P. Rosa, J.-F. Létard, G. Chastanet, *Magnetochemistry* **2016**, *2*, 15.
- [43] M. Nakaya, K. Shimayama, K. Takami, K. Hirata, A. S. Alao, M. Nakamura, L. F. Lindoy, S. Hayami, *Chem. Lett.* **2014**, *43*, 1058–1060.
- [44] K. Takahashi, K. Kawamukai, M. Okai, T. Mochida, T. Sakurai, H. Ohta, T. Yamamoto, Y. Einaga, Y. Shiota, K. Yoshizawa, *Chem. - A Eur. J.* **2016**, *22*, 1253–1257.
- [45] T. Boonprab, S. J. Lee, S. G. Telfer, K. S. Murray, W. Phonsri, G. Chastanet, E. Collet, E. Trzop, G. N. L. Jameson, P. Harding, et al., *Angew. Chem. Int. Ed.* **2019**, *58*, 11811–15.
- [46] D. Sertphon, D. J. Harding, P. Harding, K. S. Murray, B. Moubaraki, J. D. Cashion, H. Adams, *Eur. J. Inorg. Chem.* **2013**, 788–795.
- [47] M. Koike, K. Murakami, T. Fujinami, K. Nishi, N. Matsumoto, Y. Sunatsuki, *Inorg. Chim. Acta* **2013**, *399*, 185–192.
- [48] A. Tsukiashi, M. Nakaya, F. Kobayashi, R. Ohtani, M. Nakamura, J. M. Harrowfield, Y. Kim, S. Hayami, *Inorg. Chem.* **2018**, *57*, 2834–2842.
- [49] K. Takahashi, K. Yamamoto, T. Yamamoto, Y. Einaga, Y. Shiota, K. Yoshizawa, H. Mori, *Crystals* **2019**, *9*, 81.
- [50] J. K. McCusker, A. L. Rheingold, D. N. Hendrickson, *Inorg. Chem.* **1996**, *35*, 2100–2112.
- [51] M. Marchivie, P. Guionneau, J. F. Létard, D. Chasseau, *Acta Crystallogr. Sect. B Struct. Sci.* **2005**, *61*, 25–8.
- [52] R. Ketkaew, Y. Tantirungrotechai, P. Harding, D. J. Harding, M. Marchivie, **2019**, <https://octadist.github.io>.
- [53] H. Zheng, Y. S. Meng, G. L. Zhou, C. Y. Duan, O. Sato, S. Hayami, Y. Luo, T. Liu, *Angew. Chemie - Int. Ed.* **2018**, *57*, 8468–8472.
- [54] W. Phonsri, P. Harding, L. Liu, S. G. Telfer, K. S. Murray, B. Moubaraki, T. M. Ross, G. N. L. Jameson, D. J. Harding, *Chem. Sci.* **2017**, *8*, 3949–59.
- [55] A. I. Vicente, A. Joseph, L. P. Ferreira, M. de Deus Carvalho, V. H. N. Rodrigues, M. Duttine, H. P. Diogo, M. E. Minas da Piedade, M. J. Calhorda, P. N. Martinho, *Chem. Sci.* **2016**, *7*, 4251–4258.
- [56] M. S. Shongwe, U. A. Al-Zaabi, F. Al-Mjeni, C. S. Eribal, E. Sinn, I. A. Al-Omari, H. H. Hamdeh, D. Matoga, H. Adams, M. J. Morris, et al., *Inorg. Chem.* **2012**, *51*, 8241–8253.
- [57] W. Phonsri, C. G. Davies, G. N. L. Jameson, B. Moubaraki, K. S. Murray, *Chem. - A Eur. J.* **2016**, *22*, 1322–1333.
- [58] R. Bertoni, M. Lorenc, J. Laisney, A. Tissot, A. Moréac, S. F. Matar, M.-L. Boillot, E. Collet, *J. Mater. Chem. C* **2015**, *3*, 7792–7801.
- [59] A. Hauser, *Top. Curr. Chem.* **2004**, *234*, 155–198.
- [60] Rigaku, *Rigaku XRD*, Rigaku Corporation, Tokyo, Japan, **1996**.
- [61] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
- [62] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2015**, *71*, 3–8.
- [63] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339–42.

Entry for the Table of Contents



Anion effects are explored in three iron(III) spin crossover complexes with the transition temperature clearly dependent on the size and shape of the anion. One of the complexes exhibits an extremely rare light-activated spin crossover.

Institute and/or researcher Twitter usernames: @GroupHarding