Supporting Information:

Accessing Spin-Crossover Behaviour in Iron(II) complexes of N-Confused Scorpionate Ligands

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General considerations. HpzCH(OMe)$_2$ was prepared according to a literature procedure but only heating 15 h to give 70% yield (rather than reported 30 h that gave 74% yield).[^51]

Anhydrous NaH, [Fe(H$_2$O)$_6$](BF$_4$)$_2$, and all other chemicals were commercially available and were used as received. Solvents were dried by conventional drying agents and distilled under N$_2$ prior to use. The syntheses of the iron(II) complexes were carried out under an argon atmosphere using standard Schlenk techniques. After complex formation, no special precautions to avoid air were taken.

Midwest MicroLab, LLC, Indianapolis, Indiana 45250, performed all elemental analyses. Melting point determinations were made on samples contained in glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. $^1$H, and $^{13}$C NMR spectra were recorded on a Varian 400 MHz spectrometer. Chemical shifts were referenced to solvent resonances at $\delta_H$ 7.26 and $\delta_C$ 77.16 for CDCl$_3$, $\delta_H$ 2.05 for acetone-d$_6$, $\delta_H$ 1.94 and $\delta_C$ 118.26 for CD$_3$CN.

Electronic absorption (UV-Vis/NIR) measurements were made on a Cary 5000 instrument. Abbreviations for NMR and UV-Vis  br (broad), sh (shoulder), m (multiplet), ps (pseudo-), s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sept (septet). Solution magnetic moment were measured by the Evan’s method.[^52] Magnetic susceptibility data were collected on a Quantum Design MPMS3 SQUID magnetometer. Raw moment data were corrected for sample shape and radial offset corrections using the MPMS 3 Sample Geometry Simulator.[^53]

Diamagnetic corrections of -365x10$^{-6}$ emu/mol for 1, -522.5x10$^{-6}$ emu/mol for 2, 325x10$^{-6}$ emu/mol for 3, and -27.8 x10$^{-6}$ for CH$_3$CN calculated from tabulated Pascal’s constants[^54] were applied to the measured susceptibility data, as appropriate.
A. Ligand Syntheses.

**BnpzCH(OMe)₂, A.** Under argon, HpzCH(OMe)₂ (4.38 g, 30.8 mmol) was added dropwise to a suspension of NaH (0.890 g, 37.1 mmol) in 50 mL THF. The solution was allowed to stir at room temperature for 1 h then benzyl bromide (4.03 mL, 33.9 mmol) was added all at once via syringe and the contents were stirred at room temperature 15 h. Solvent was removed by vacuum distillation, then water (75 mL) and ethyl acetate (75 mL) were used to transfer the contents of the reaction vessel to a separatory funnel. The water layer was extracted with ethyl acetate a total of 3 times (75 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo* to give 6.82 g (95% yield, if pure) of the desired product as a red oil sufficiently pure to be used successfully in the following step. If desired, the pure compound can be obtained as a yellow oil after separation by column chromatography using silica gel as the stationary phase and hexane/ethyl acetate (1:1 v/v) as the eluent (Rᵢ = 0.69, stained with I₂, not UV active). ¹H NMR (CDCl₃) δ_H: 7.31 (m, 4H), 7.19 (m, 2H), 6.33 (d, J = 2.3 Hz, 1H, H₄pz), 5.51 (s, 1H, CHOMe₂), 5.32 (s, 2H, CH₂), 3.39 (s, 6H, OCH₃). ¹³C NMR (CDCl₃) δ_C: 150.1, 136.5, 130.1, 128.9, 128.2, 127.8, 104.6, 99.8, 56.1, 53.1 ppm.

**BnpzCH(pz)₂, BN.** A mixture of 0.703 g (3.03 mmol) A, 0.412 g (6.10 mmol) pyrazole, 0.029 g (0.15 mmol, 5 mol %), p-toluenesulfonic acid monohydrate, and 5 mL C₆H₆ were placed in a round bottom flask with a magnetic stirbar. The flask was connected to a distillation apparatus under argon and was heated until most of the volatiles (C₆H₆, MeOH) had distilled, as indicated by a drop in distillate temperature (do no overheat!). Residual solvent was removed via vacuum distillation at room temperature. Then, water (50 mL) and ethyl acetate (50 mL) were used to transfer the contents of the reaction vessel to a separatory funnel and the layers were
separated. The aqueous layer was extracted with three more 50 mL portions of ethyl acetate. The combined organic layers were dried over MgSO$_4$, filtered, and solvent was removed in vacuo. The crude product mixture was separated using column chromatography [silica gel, eluent of hexane:ethyl acetate (1:1)]. The product eluted in a yellow band ($R_f = 0.56$, stained with I$_2$) which after rotary evaporation of eluent gave a yellow oil that solidified under vacuum. The product was then purified by cooling a concentrated Et$_2$O solution to -30°C for 3 h, filtering the crystals, and drying under vacuum to yield a colorless solid (0.66 g, 2.39 mmol, 72% yield).

**TspzCH(OMe)$_2$, B.** *(a) Small scale preparation with column chromatography purification.* A 2.30 g (16.2 mmol) HpzCH(OMe)$_2$ was added to a stirred suspension of NaOH (1.95 g, 48.63 mmol) in DCM (100 mL) and stirred at room temperature for 10 minutes. The reaction vessel was then placed in an ice bath and p-toluenesulfonylchloride, TsCl, (7.42 g, 38.9 mmol) was added slowly over 10 minutes. The reaction was stirred at room temperature for 15 hours. Then, the contents of the reaction vessel were transferred to a separatory funnel. The water layer was extracted with DCM a total of 3 times (100 mL each). The combined organic layers were dried over MgSO$_4$, filtered, and solvent was removed in vacuo. The crude reaction mixture was loaded onto a column containing silica gel and eluted using a hexane/ethyl acetate (3:1) solution to remove excess TsCl ($R_f = 0.57$) before switching to pure ethyl acetate to elute the desired product ($R_f = 0.82$) as a colorless solid (3.57g, 12.05 mmol, 74% yield).
(b) Large Scale preparation, purification without column chromatography. A suspension of 16.65 g (117.1 mmol) HpzCH(OMe)₂, 14.06 g (351.4 mmol) NaOH, and 22.33 g (117.1 mmol) TsCl in 250 mL CH₂Cl₂ are mixed as above, after workup (three 100 mL portions CH₂Cl₂ used for extraction). The product is obtained from the evaporated organic fraction by triturating with ca. 100 mL diethyl ether and filtering to isolate the poorly soluble desired product. In two successive extractions, the volume of the Et₂O soluble portion is reduced by half and the insoluble portion is collected. Total 17.78 g (51% yield). If desired, the product may be recrystallized by cooling a boiling supersaturated heptane solution to room temperature. Mp, 84-85°C. ¹H NMR (CDCl₃) δH: 8.05 (d, J = 2.8 Hz, 1H, H₄Pz), 7.88 (d, J = 8.4 Hz, 2H, Ar-H), 7.31 (d, J = 8.4 Hz, Ar-H), 6.47 (d, J = 2.8 Hz, 1H, H₅Pz), 5.35 (s, 1H, CHOMe₂), 3.32 (s, 6H, OCH₃), 2.41 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃) δC: 156.0, 145.9, 134.0, 132.0, 130.0, 128.1, 107.2, 99.3, 53.6, 21.7 ppm.

TspzCH(O), C. A magnetically stirred mixture of 16.34 g (55.13 mmol) B, 0.21 mL (2.8 mmol) trifluoroacetic acid, 150 mL THF, and 50 mL H₂O was heated at reflux for 21 h. After cooling to room temperature, the mixture was neutralized by adding saturated NaHCO₃ (aq) (ca. 100 mL). Then, after gas evolution ceased, the organic and aqueous phases were separated and the aqueous layer was extracted with three 150 mL portions ethyl acetate. The organic phases were combined, dried over MgSO₄, filtered, and solvent was removed by rotary evaporation. Approximately 400 mL heptane was added, the mixture was heated to reflux, and then the hot solution was decanted from the red oil. Cooling the solution to -30°C for 1 h produced a pale yellow solid of C that was isolated by vacuum filtration, washing with ice cold hexane, and subsequent drying under vacuum. Yield: 10.09 g, 45.4 mmol, 82 %. Mp, 92-94°C. ¹H NMR
(CDCl\textsubscript{3}) \( \delta \): 9.97 (s, 1H, CHO), 8.15 (d, \( J = 2.8 \) Hz, 1H, H\textsubscript{3}Pz), 7.96 (d, \( J = 8.4 \) Hz, 2H, Ar-H), 7.38 (d, \( J = 8.4 \) Hz, 2H, Ar-H), 6.84 (d, \( J = 2.8 \) Hz, 1H, H\textsubscript{4}Pz), 2.45 (s, 3H, CH\textsubscript{3}) ppm. \(^{13}\text{C} \) NMR (CDCl\textsubscript{3}) \( \delta \text{C} \): 186.0, 154.8, 146.9, 132.9, 132.5, 130.3, 128.5, 106.9, 21.8 ppm.

\textbf{TspzCH(pz)}\textsubscript{2}, \( ^{13}\text{L} \). Under argon, a solution of 3.12 g (45.8 mmol) H-pyrazole in 25 mL THF was transferred slowly over 5 minutes via cannula to a suspension of 1.10 g (45.8 mmol) NaH in 40 mL THF. To ensure quantitative transfer, the flask originally containing pyrazole was rinsed with THF and the washings transferred to the reaction mixture (2x2.5 mL). After the resulting solution had been stirred until \( \text{H}_{2} \) evolution ceased (about 5 minutes), SOCl\textsubscript{2} (1.67 mL, 22.9 mmol) was added by syringe slowly over 5 minutes; a precipitate formed during the addition. The suspension was stirred at room temperature for 10 minutes, then 0.1 g (0.76 mmol) CoCl\textsubscript{2} (s) was added under an argon blanket. After the blue suspension had been stirred 2 min, a solution of 3.39 g (15.3 mmol) C in 25 mL THF was transferred to the reaction mixture via cannula (aided by two 2.5 mL THF washings, as above). The reaction mixture was heated at reflux under argon for 15 h, and then was cooled to room temperature. Solvent was removed by vacuum distillation, 100 mL each \( \text{H}_{2} \text{O} \) and ethyl acetate was added. The aqueous and organic phases were separated and the aqueous layer was extracted with three 100 mL portions ethyl acetate. The combined organic layers were dried over MgSO\textsubscript{4}, filtered, and solvent was removed by rotary evaporation. The crude reaction mixture was dry loaded onto a column of silica gel. Two unidentified impurities were eluted using a hexane/diethyl ether (1:2) \( R_{f}'s \) 0.6 and 0.37, respectively). Pure ethyl acetate was then used to elute the desired product \( R_{f} = 0.82 \). After removing solvent from the desired band, triturating with \( \text{Et}_{2} \text{O} \), and drying under vacuum, 4.65 g (12.6 mmol, 83% yield) \( ^{13}\text{L} \) was obtained as a colorless solid.
Alternatively, column chromatography can be avoided and the product can purified either by Soxhlet extraction for 8 hr with boiling heptane (72% yield) or even slightly lower yield (58%) by adding 100 mL heptane to the evaporated ethyl acetate extracts, heating at reflux 5 min, cooling the decanted hot heptane solution to room temperature, filtering the crystalline product, and drying under vacuum. This extraction/crystallization process is then repeated two more times. Mp, 114-116. \(^1\)H NMR (CDCl\(_3\)) \(\delta\): 8.11 (d, \(J = 2.8\) Hz, 1H, H\(_{5}\) Pz-NC), 7.87 (d, \(J = 8.3\) Hz, 2H, Ar-H), 7.66 (s, 1H, CHPz\(_2\)), 7.56 (m, 4H, H\(_3\)Pz and H\(_5\)Pz), 7.32 (d, \(J = 8.3\) Hz, 2H, Ar-H), 6.54 (d, \(J = 2.8\) Hz, 1H, H\(_4\)Pz-NC), 6.28 (m, 2H, H\(_3\)Pz), 2.43 (s, 3H, CH\(_3\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\): 152.6, 146.3, 141.0, 133.5, 132.3, 130.1, 129.6, 128.4, 108.8, 106.7, 72.5, 21.8 ppm.

\textbf{HpzCH(pz)\(_2\), \(\text{H}^L\).} A mixture of 10.0 g (27.1 mmol) \(\text{TsL}\), 40.0 mL 5.00 \(M\) (200 mmol) NaOH (aq), and 70 mL THF was heated at reflux until TLC showed \(\text{TsL}\) had been consumed (10 min). THF was then removed by vacuum distillation. The product mixture was partitioned between 50 mL CH\(_2\)Cl\(_2\) and 50 mL H\(_2\)O. The organic and aqueous phases were separated. The aqueous layer was extracted with twelve 75 mL portions CH\(_2\)Cl\(_2\) then four 50 mL portions ethyl acetate. The combined organic layers were dried over MgSO\(_4\), filtered, and solvent was removed by rotary evaporation. The desired product has low solubility in benzene (50 mL/ g), so a minimum amount of benzene (300 mL) is added such as to form a solution when heated at reflux. Cooling the boiling benzene solution to room temperature, filtering, and drying the colorless crystals under vacuum gave 4.67 g (80 % yield) \(\text{H}^L\). Mp, = 138-140\(^\circ\)C. \(^1\)H NMR (CD\(_2\)Cl\(_2\)) \(\delta\): 11.04 (br s, 1H, NH), 7.78 (s, 1H, C\(_{\text{meth}}\)H), 7.66 (d, \(J = 2.5\) Hz, 2H, H\(_3\)Pz), 7.58 (d, \(J = 2.4\) Hz, 1H, H\(_5\)Pz-NC), 7.56 (m, 2H, H\(_5\)Pz), 6.39 (d, \(J = 2.4\) Hz, 1H, H\(_4\)Pz-NC), 6.30 (m, 2H, H\(_3\)Pz) ppm. \(^{13}\)H NMR (acetone-d\(_6\)) \(\delta\): 7.86 (dd, \(J = 2.4, 0.7\) Hz, 2H), 7.83 (s, 1H), 7.77 (d, \(J = 2.2\) Hz, 1H), 7.45 (dd, \(J = 1.8, 0.7\) Hz,
$^{13}$C NMR (CD$_2$Cl$_2$) $\delta_C$: 140.5, 130.7 (br, overlapping signals), 130.2, 106.6, 105.5, 74.0 ppm.

B. Syntheses of Metal Complexes.

[Fe($^{8n}$L)$_2$](BF$_4$)$_2$, 1. Under argon, a solution of 0.660 g (2.17 mmol) $^{8n}$L in 10 mL THF was added to a solution of 0.366 g (1.08 mmol) [Fe(H$_2$O)$_6$](BF$_4$)$_2$ in 10 mL THF. A colorless solid precipitated almost instantly on mixing reagents. The flask originally containing $^{8n}$L was washed with 5 mL THF and transferred to the reaction mixture to ensure quantitative transfer. The suspension was stirred for 1 h and the colorless solid was collected by cannula filtration. The solid was washed with two 2 mL portions of THF, 2 mL Et$_2$O, and was dried under vacuum to give 0.678 g (75% yield) 1 as a colorless solid. Mp, > 250°C. Anal. Calcd. (found) for C$_{34}$H$_{32}$N$_{12}$B$_2$F$_8$Fe: %C 48.72 (48.50), %H 3.85 (3.81), %N 20.05 (19.99). $\mu_{eff}$ (CH$_3$CN, Evans)= 5.1 $\mu_B$. $^1$H NMR (CD$_3$CN) $\delta_H$: 50.9 (br s), 45.9 (br s), 41.3 (br s), 14.2 (br s), 11.0 (br s), 10.7 (br s), 10.4 (br s), 7.3 (br s), 3.5 (br s), 2.2 (br s) ppm. . UV-vis (CH$_3$CN, $\lambda$ nm, $\varepsilon$ M$^{-1}$cm$^{-1}$): 222 (45,000), 766 (3). X-Ray quality crystals of 1·2CH$_3$CN were grown by slow vapor diffusion of Et$_2$O into an acetonitrile solution of the complex. Solvent is readily removed under vacuum.

[Fe($^{Ts}$L)$_2$](BF$_4$)$_2$, 2. A solution of 0.195 g (0.530 mmol) $^{Ts}$L in 5 mL THF was added to a solution of 0.0890 g (0.265 mmol) [Fe(H$_2$O)$_6$](BF$_4$)$_2$ in 5 mL THF. An additional 3 mL THF was used to ensure quantitative transfer of $^{Ts}$L to the reaction mixture. The mixture was stirred at room temperature for 16 h, during which time a colorless solid formed that was collected by cannula filtration. The solid was washed with two 2 mL portions of THF, 2 mL Et$_2$O, and was dried under vacuum to give 0.22 g (86% yield) 2 as a colorless solid. Mp, > 250°C. Anal. Calcd. (found) for
C_{34}H_{32}N_{12}B_{2}F_{8}FeO_{5}S_{2}: \%C 42.26 (42.40), \%H 3.34 (3.37), \%N 17.39 (17.25). \mu_{\text{eff}} (\text{CH}_3\text{CN}, \text{Evans}) = 5.1 \mu_\text{B}. \text{^1H NMR} (\text{CD}_3\text{CN}) \delta_{\text{H}}: 49.8 (\text{v. br. s}), 8.11 (\text{v. br. s}), 3.65 (\text{br. s}), 3.25 (\text{v. br. s}), 1.81, 1.25 (\text{v. br. s}) \text{ ppm}. \text{UV-vis} (\text{CH}_3\text{CN}, \lambda \text{ nm}, \epsilon \text{ M}^{-1}\text{cm}^{-1}): 223 (43,700), 243 (38,000), 306 (sh, 2400), 806 (12). X-ray quality crystals of 2·2CH_3\text{CN} were grown by slow vapor diffusion of Et_2O into an acetonitrile solution of the complex. Solvent is readily lost by washing crystals with Et_2O, drying under N_2, and grinding. It is noted that an air-dried sample of the THF precipitate from the original reaction without Et_2O washing or vacuum drying analyzed as 2·THF·H_2O; Anal. Calcd. (found) for C_{38}H_{42}N_{12}B_{2}F_{8}FeO_{5}S_{2}: \%C 43.20 (43.07), \%H 4.01 (3.72), \%N 15.91 (15.76); so drying under vacuum or washing with Et_2O and subsequent drying under an inert gas stream is required to give solvate-free samples.

\[[\text{Fe}({^4}\text{L})_2]([\text{BF}_4])_2, 3\]. A solution of 0.122 g (0.362 mmol) [Fe(\text{H}_2\text{O})_6][\text{BF}_4]_2 in 5 mL acetone was added to a solution of 0.264 g (1.23 mmol) \text{^4L} in 5 mL acetone, a pink solution and precipitate formed immediately on mixing. After the pink suspension had been stirred 15 h, the solid was collected by filtration, washed with two 3 mL portions acetone, one 3 mL portion Et_2O, and dried under vacuum. Yield: 0.385 g, 95%. Mp, becomes colorless by 150^\circ\text{C}, did not melt below 250^\circ\text{C}. Anal. Calcd. (found) for C_{20}H_{20}N_{12}B_{2}F_{8}\text{Fe}: C, 36.51 (36.72); H, 3.06 (3.05); N, 25.55 (25.54). \mu_{\text{eff}} (\text{CH}_3\text{CN}, \text{Evans})= 3.4 \mu_\text{B}. \text{^1H NMR} (\text{CD}_3\text{CN}) \delta_{\text{H}}: 24.6 (\text{v. br. s}), 18.6 (\text{v. br. s}), 18.4 (\text{v. br. s}), 17.8 (\text{v. br. s}), 17.1 (\text{v. br. s}), 16.3 (\text{v. br. s}), 15.9 (\text{v. v. br. s}), 10.5 (\text{v. br. s}), 10.1 (\text{v. br. s}), 7.6 (\text{v. br. s}), 7.4 (\text{v. br. s}), 2.16 (\text{s}), 2.09 (\text{s}), -4.8 (\text{v. br s}) \text{ ppm}. \text{UV-vis} (\text{CH}_3\text{CN}, \lambda \text{ nm}, \epsilon \text{ M}^{-1}\text{cm}^{-1}): 271 (4300), 314 (sh, 5900), 331 (7300), 369 (sh, 430), 528 (54), 794 (1). Solubility @ 295K: ca. 8 mg/mL CH_3\text{CN}.
**Crystallography.** X-ray intensity data from a colorless needle of 1·2CH$_3$CN were collected at 100.0(1) K while that from a colorless prism of 2·2CH$_3$CN were collected at 99.8(4) K with an Oxford Diffraction Ltd. Supernova equipped with a 135 mm Atlas CCD detector, by using Cu Kα radiation, $\lambda = 1.54184$ Å for the former two experiments and for 3, but Mo Kα (0.70173 Å) for 2·2CH$_3$CN. Raw data frame integration and Lp corrections were performed with either CrysAlis Pro (Oxford Diffraction, Ltd.)$^{[S5]}$ or SAINT+ (Bruker).$^{[S6]}$ Final unit cell parameters were determined by least-squares refinement of 8357 reflections from the data set of 1·2CH$_3$CN, 10831 reflections from data set of 2·2CH$_3$CN and of 6136 reflections from data set of 3, with I $> 2\sigma$(I) for all cases. Analysis of the data showed negligible crystal decay during collection in each case. Direct methods structure solutions were performed with Olex2.solve$^{[S7]}$ while difference Fourier calculations and full-matrix least-squares refinements against F2 were performed with SHELXTL.$^{[S8]}$ Empirical absorption corrections were applied using spherical harmonics implemented in the SCALE3 ABSPACK scaling algorithm. The structure of 2·2CH$_3$CN has one heavily disordered BF$_4$ anion (with central B2) whose atoms were refined with isotropic displacement parameters. The disorder is complicated as the anion(s) is(are) located on a two-fold axis and has four components: component #1 consists of B2, F3, F4, F5 which by crystallographic 2-fold axis gives component #2. Component #3 has B2, F6, F6 (over 2-fold axis), F7, and F8 which by reflection about the 2-fold axis gives component #4 with positions of F6 of each coinciding. Also, the acetonitrile solvate molecule is disordered and the nitrogen N7a was refined with isotropic displacement parameters. The remaining non-hydrogen atoms were refined with anisotropic displacement parameters. For 3, the crystal of a pink needle is a twin (rotation 180° around x). The dication in 3 is positioned on a crystallographic inversion
center and, as such, it is supposed to be a trans- isomer. However, a detailed analysis shows that the pyrazol-3-yl ring (N5...C10) is interchangeably superimposed with one of pyrazol-2-yl rings (N3...C7) in a 64:36 ratio. This disorder apparently correlates with disorder of BF$_4^-$ counterion, which populates two nearby positions in a 65:35 ratio, and makes H-bonds with N-H groups of the dication. The disorder can be result of (a) superposition of two trans- isomeric dications rotated by 120° around the pseudo-3-fold axis of the complex, (b) superposition of the trans-isomer with racemic mixture of superimposed cis- isomers, or anything in-between, including (c) a hypothetical 1:1 mixture of trans- and cis- isomers. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The X-ray crystallographic parameters and further details of data collection and structure refinements are presented in Table S1.
Table S1. Crystallographic data collection and structure refinement for 1·2CH\textsubscript{3}CN, 2·2CH\textsubscript{3}CN and 3.

<table>
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<th>Compound</th>
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<th>2·2CH\textsubscript{3}CN</th>
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<td>4228 (R\textsubscript{int} 0.0385)</td>
<td>5524 (R\textsubscript{int} 0.0329)</td>
<td>5451 (R\textsubscript{int} 0.000)</td>
</tr>
<tr>
<td>T\textsubscript{min}/max</td>
<td>0.524 / 0.871</td>
<td>0.828/0.932</td>
<td>0.520/0.921</td>
</tr>
<tr>
<td>Data/restraints/ parameters</td>
<td>4228/0/287</td>
<td>5524/3/342</td>
<td>5451/30/244</td>
</tr>
<tr>
<td>Goodness-of-fit on F\textsuperscript{2}</td>
<td>1.054</td>
<td>1.036</td>
<td>1.048</td>
</tr>
<tr>
<td>R1/\textit{w}R2(\textit{F}2&gt;2\sigma(\textit{F}))\textsuperscript{a}</td>
<td>0.0380/0.1041</td>
<td>0.0390/0.0860</td>
<td>0.0454/0.1233</td>
</tr>
<tr>
<td>R1/\textit{w}R2 (all data)\textsuperscript{a}</td>
<td>0.0430/0.1088</td>
<td>0.0518/0.0949</td>
<td>0.0495/0.1257</td>
</tr>
<tr>
<td>Largest diff. peak/hole / e Å\textsuperscript{-3}</td>
<td>0.43/-0.43</td>
<td>0.52/-0.52</td>
<td>0.56/-0.52</td>
</tr>
</tbody>
</table>

\textsuperscript{a} R1 = \Sigma||F\textsubscript{o}|| - |F\textsubscript{c}||/ \Sigma|F\textsubscript{o}|, \textit{w}R2 = [ \Sigma \textit{w}((|F\textsubscript{o}| - |F\textsubscript{c}|)^2/\Sigma \textit{w}|F\textsubscript{o}|^2)]^{1/2}. 
Figure S1. Top: Major disorder component of 3. Bottom: View down b- of packing with unit cell outlined and disorder components shown.
Figure S2. Variable temperature magnetic data on 1 (top) and 2 (bottom) acquired with a SQUID magnetometer.

\[ \text{[Fe}^{(\text{Bn} L)_{2}}(\text{BF}_4)_2, \ 1 \]

\[ \text{[Fe}^{(\text{Ts} L)_{2}}(\text{BF}_4)_2, \ 2 \]

\[ \mu_{\text{eff}}/\mu_B \]

\[ T \text{ (K)} \]
Figure S3. Top: \textit{d-d} region of electronic spectrum of 1 in CH$_3$CN. Bottom: Electronic spectrum of 2 in CH$_3$CN where inset shows \textit{d-d} region.
Figure S4. Electronic spectra of 3 in CH$_3$CN. Top left: Experimental (blue line), Gaussian fits (black dashed lines), and sum of Gaussian bands (red line). Top right: d-d region showing bands for HS and LS Fe(II). Bottom: Spectra at various temperature between 243 (thick blue line) to 343 K (thick red line).
Figure S5. Paramagnetic $^1$H NMR spectra of 1 (top), 2 (middle), 3 (bottom) in CD$_3$CN acquired at 295 K.
Figure S6. Top: Variable temperature $^1$H NMR spectrum of 3 in CD$_3$CN in 20 K increments from 323 K (top) to 243 K (bottom). Bottom Left: Solution magnetic moment as a function of temperature (Evan’s method) in the range above plus one measurement at 295 K. Bottom right: Plot of chemical shift of most upfield and downfield resonances as a function of solution magnetic moment determined by Evan’s method (from 243 to 323 K), showing linear correlation.
Figure S7. Supramolecular structure of 1·CH$_3$CN. (a) List of short contacts. (b) Two views of short contacts [cyan lines (Σvdw – 0.1 Å)] with atom labelling shown in perspective (left) and down c- with unit cell outlined (right). (c) View of two sheets stacked along a-axis (red axis), solvent shown in black.

(a) Donor(D)-X···Acceptor(A) | D-X (Å) | X···A (Å) | D···A (Å) | D-X···A (°) 
---|---|---|---|---
C2-H2···F4 | 0.95 | 2.48 | 3.323(2) | 148
C4-H4···F1 | 1.00 | 2.34 | 3.279(2) | 155
C4-H4···F2 | 1.00 | 2.30 | 3.179(2) | 146
C19-H19a···F3 | 0.98 | 2.35 | 3.318(3) | 170
C19-H19b···N7 | 0.98 | 2.59 | 3.361(4) | 136
C21-H21···F4 | 0.95 | 2.49 | 3.132(2) | 125
C22-H22···F3 | 0.95 | 2.53 | 3.361(2) | 146
C32-H32···F2 | 0.95 | 2.53 | 3.352(2) | 145
C36-H36···F1 | 0.95 | 2.54 | 3.275(2) | 134

Ct(i) = centroid of ring containing atom i, γ = Angle Ct(i)-Ct(j) and normal to plane containing Ct(j);
Figure S8. Views of the structure of 2·2CH$_3$CN. Top: Asymmetric unit with hydrogens removed for clarity. Bottom: Views showing disposition of the tosyl groups with acetonitrile molecules removed for clarity.

Selected bond distances (Å): Fe1-N2 2.4055(14), Fe1-N11 2.1227(14), Fe1-N21 2.1156(14), S1-N1 1.7015(15), S1-O1 1.4255(14), S1-O2 1.4194(14); and bond angles (°): N21 Fe1 N21 179.998(1), N11 Fe1 N11 179.999(2), N2 Fe1 N2 179.999(1), N21-Fe1-N11 87.92(5), N21-Fe1-N11 92.08(5), N21-Fe1-N11 92.08(5), N21-Fe1-N2 99.00(5), N21-Fe1-N21 81.00(5), N11-Fe1-N2 81.54(5), N11-Fe1-N21 98.46(5).

$^{1}$3/2-X,3/2-Y,1-Z;
Figure S9. Magnetic measurements made on samples of “1·2CH$_3$CN” treated by various evacuation times prior to measurements. From top to bottom at 30 K: Evacuated overnight (red line, same as Fig S2, top), evacuated 2 hr (orange square markers), sample blown dry with N$_2$ then evacuated in “air-tight” sample holder in magnetometer 20 min (cyan triangles); sample blown dry with N2 then evacuated in “air-tight” sample holder in magnetometer 5 min (green line, same as Figure 4 in main text).
References:


